REMOVAL OF LEAD & CHROMIUM FROM WATER USING MODIFIED & NONMODIFIED CARBON NANOTUBES

BY

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This thesis, written by **Omer Yahya Mohammed Bakather** under the direction of his thesis advisor and approved by his thesis committee, has been presented to and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN CHEMICAL ENGINEERING.**

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This work is dedicated to my beloved **parents**, my **wife**, my **brothers**, my **sister** and my **children** : ***Mohammad*** and ***Elaf***.

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ABSTRACT

Full Name	**OMER YAHYA MOHAMMAD BAKATHER**
Title of Study	**REMOVAL OF LEAD & CHROMIUM FROM WATER BY USING MODIFIED & NONMODIFIED CARBON NANOTUBES**
Major Field	**CHEMICAL ENGINEERING**
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This study was carried out to evaluate the environmental application of carbon nanotubes through the experiment removal of chromium trivalent Cr (III) and lead divalent Pb(II) from water by using carbon nanotubes. The matrix design has been developed in this experimental runs in order to find the optimal condition of the Pb (II) and Cr (III) removal from water. To achieve the objectives of the study, four independent variables including pH, adsorbent dosage, time contact and its agitation speed were carried out to determine the influence of these parameters on the adsorption capacity of the chromium and lead. Multi wall carbon nanotubes (MWCNTs) were characterized by filed emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) in order to measure the diameter and the length of the adsorbent. The diameter of the carbon nanotubes were varied from 20-40 nm with average diameter at 24 nm and 10-micrometer in length. Adsorption isotherms were used in order to model the adsorption behavior and to calculate the adsorption capacity of the absorbents. The results showed

that, 100 % of Pb (II) removal was achieved while 18 % of Cr (III) was removed from water by using modified carbon nanotubes (M-CNTs) at pH 7, 150 rpm and 2 hours. These high removal efficiencies were likely attributed to the strong affinity of lead and chromium ions to the physical and chemical properties of the CNTs. The adsorption isotherms plots were well fitted with experimental data.

THESIS ABSTRACT (ARABIC)

ملخص الرسالة

الإســـــــــم: عـــمر يحـــــــيى محـمد باكـــثير

عنوان الرسالة: ازالة الرصاص والكرميوم من الماء باستخدام انابيب الكاربون النانونية المتغيرة وغير المتغيرة

التخصـــــص: هندســـة كيميـــــائية

هذه الدراسة اجريت لدراسة استخدام انابيب الكربون النانونية في ازالة الكرميوم ثلاثي التكافؤ والرصاص ثنائي التكافؤ.

مصفوفة التجارب طورت للحصول على الشروط المثالية لزالة الكرميوم ثلاثي التكافؤ والرصاص ثنائي التكافؤ. لاجل هذه الاهداف هناك اربعة عناصر متغيرة وهي الرقم الهيدروجيني وكمية المادة المازة والزمن وسرعة الخلط درست من اجل تحديد السعة الامتصاصية لكل من الكرميوم ثلاثي التكافؤ والرصاص ثنائي التكافؤ.

ايضا انابيب الكربون النانونية فحصت باستخدام الماسح الالكتروني الميكروسكوبي والناقل الالكتروني الميكروسكوبي وذلك لقياس القطر والطول لهذه الانابيب .قطر الانابيب بلغ حوالي من 20 الى 40 نانوميتر ومتوسط القطر حوالي 24 نانوميتر اما الطول فكان حوالي 10 ميكرميتر.

نماذج الامتصاص ذات درجة الحرارة الثابتة استخدمت لحساب سعة المادة المازة (انابيب الكربون النانونية). وقد اظهرت النتائج ان نسبة ازالة الرصاص هي 100 % بينما كانت للكرميوم 18 % وذلك باستخدام انابيب الكربون النانونية المتغيرة عند الرقم الهيدروجيني 7 وسرعة الخلط 150 دورة بالدقيقة خلال زمن قدره ساعتين. وقد كانت دقة هذه النماذج متطابقة تماما مع التجارب التي اجريت .

MASTER OF SCIENCE

KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS

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CHAPTER I

INTRODUCTION

1.1 General Introduction

In the resent years, nanotechnology has become one of the most important and exciting forefront fields in chemistry, physics engineering and biology. Research on new materials technology is attracting the attention of researchers all over the world. Developments are being made to improve the properties of the materials and also to find alternative precursors that can bestow desirable properties on the materials. Nanotechnology, which is one of the new technologies, refers to the development of devices, structures, and systems whose size varies from 1 to 100 nanometers (nm). The last decade has seen advancement in every side of nanotechnology such as: nanoparticles and powders; nanolayers and coats; electrical, optic and mechanical nanodevices; and nanostructured biological materials. Presently, nanotechnology is estimated to be influential in the next 20-30 years, in all fields of science and technology (Harris, 2001).

Great interest has recently been developed in the area of nanostructures carbon materials. Carbon nanostructure materials are becoming of considerable commercial importance with interest growing rapidly over the decade or so since the discovery of buckminsterfullerene, carbon nanotubes, and carbon nanofibers (Dresselhaus et al.,

2001). Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) are among the most eminent materials in the first rank of revolution nanotechnology. The most features of these structures are their electronic, mechanical, optical eye-catching and chemical characteristics, which open a way to future applications. These properties can even be measured on single nanotubes and nanofiber. For commercial application, large quantities of purified carbon nanotubes are needed (Dresselhaus et al., 1998; Thomas, 1997).Carbon nanotubes (CNTs), a member in carbon family, have novel properties that make them potentially useful in many applications in nanotechnology, electronics, optics, water treatment and other fields of materials science. Since their discovery in 1991 (Iijima, 1991), carbon nanotubes (CNTs) have attracted considerable researchers' interest due their exceptional mechanical electrical properties, highly chemical stability and large specific area.

One of their important applications is water treatment to remove inorganic and organic pollutants. Increase of heavy metals in water is due to the growth of the industrial countries .The presence of heavy metals such as cd^{2+} ,Pb^{2+} ,Cu^{2+} ,Cr^{6+} ,Ni^{2+} and so on ,are toxic to human, animals and plants beings because of their cumulative and interfering effects on bio-chemical functions of beings′s cells. The main sources of theses metals are metallurgical, tannery, chemical manufacturing, mining battery manufacturing industries, etc (Nordberg et al., 2007).

1.2 Significance of Study

Carbon nanotubes can be applied in various fields, one of which is in the environmental field especially regarding the wastewater treatment. Since there is no much study has been done to develop carbon nanotubes as a competent adsorbent and the conditions required for optimum removal of heavy metals are still in vague. This study is to investigate the roles of carbon nanotubes in preserving our environment to be free from pollution, for the safety, health and public welfare.

1.3 Objective of the Study

The objectives of this research can be summarized as follows:

1. To remove lead (Pb^{+2}) and chromium (Cr^{+3}) by using raw and modified CNTs.
2. To optimize the process parameters such as pH, dosage of CNTs, agitation speed and contact time in order to maximize the removal of lead and chromium.
3. To study the kinetics adsorption isotherms using Langmuir and Freundlich adsorption isotherms.

CHAPTER II

LITERATURE REVIEW

2.1 History of Carbon Nanotubes

Carbon nanotubes are extremely long, thin cylinders of graphite, with at least one end typically capped with hemisphere of buckyball structure belong to the fullerene family of carbon allotropes were discovered in 1991 by Sumio Ijima of NEC Laboratory in Tsukuba, Japan using arc-discharge method and High-Resolution Transmission Electron Microscope (HRTEM) for characterization (Iijima, 1991). Since then, an enormous interest has been developed in the area of carbon nanotubes productions and its applications. This is due to the uniqueness of its electronic and mechanical properties.

2.2 Types of Carbon Nanotubes

Nanotubes are categorized as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Most single-walled carbon nanotubes (SWCNT) have a diameter close to 1 nanometer, with a tube length that can be many thousands of times longer. The structure of a SWCNT can be conceptualized by wrapping a one-atom-thick layer of graphite called graphene into a seamless cylinder. The way the graphene sheet is wrapped is represented by a pair of indices (n,m) called the chiral vector. The

integers n and m denote the number of unit vectors along two directions in the honeycomb crystal lattice of graphene. If m=0, the nanotubes are called "zigzag". If n=m, the nanotubes are called "armchair". Otherwise, they are called "chiral as shown in Figure 2.1

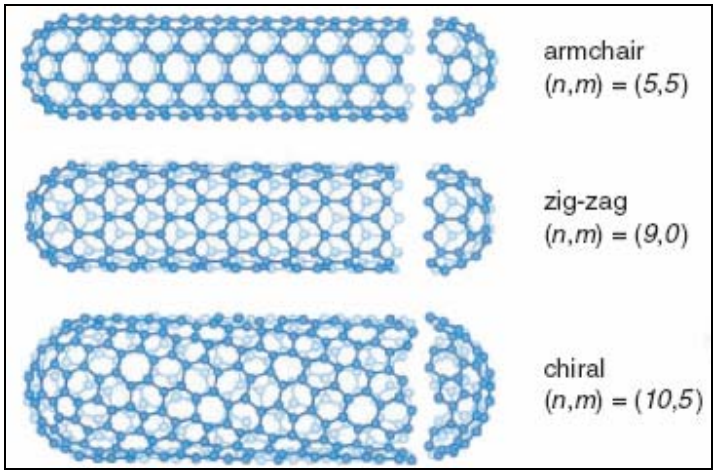


Figure 2. 1 : Types of carbon nanotubes structures courtesy (Bekyarova et. al, 2005)

Multi walled carbon nanotubes (MWCNTs) can be considered as a collection of concentric SWCNTs with different diameters as shown in Figure 2.2. The length and diameter of these structures differ a lot from those of SWCNTs and their properties are also very different. The first production of (MWCNTs) was developed in 1992 by Ebbesen and Ajayan (Ebbesen and Ajayan, 1992).

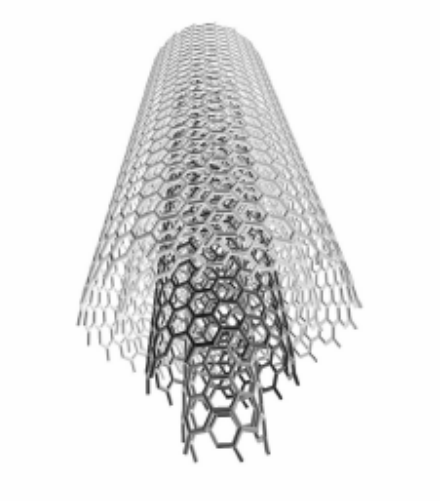


Figure 2. 2 : Schematic theoretical model for multi-walled carbon nanotubes

2.3 Properties of Carbon Nanotubes

2.3.1 Mechanical Properties

Carbon nanotubes are considered the strongest and stiffest materials on earth, in terms of tensile strength and elastic modulus respectively. This strength results from the covalent sp^2 bonds formed between the individual carbon atoms. The (CNTs) have the highest Young's modulus of all different types of composite tubes such as BN, BC_3, BC_2N, C_3N_4, CN, etc as shown in TABLE 2.1. Experimental and theoretical results have shown an elastic modulus of greater than 1 TPa (that of a diamond is 1.2 TPa) and have reported

strengths 10–100 times higher than the strongest steel at a fraction of the weight (Thoteson et al., 2001).

TABLE 2. 1: Mechanical properties of carbon nanotubes (Yamabe, 1995)

Material	Young's modulus (GPa)	Tensile strength (GPa)	Density (g/cm3)
SWCNT	1054	150	
MWCNT	1200	150	2.6
Steel	208	0.4	7.8
Epoxy	3.5	0.005	1.25
Wood	16	0.008	0.6

Carbon nanotube is very flexible .It can be elongated, twisted, flattened, or bent into circles before fracturing. The elastic modulus, Poisson's ratio and bulk modulus were all found to be directly affected by the tubes radius. A max bulk modulus was found to be 38 GPa with samples having a radius of 0.6 nm. For multi-wall nanotubes the properties were a little more complicated to calculate (Paradise and Goswami, 2007).

2.3.2 Thermal Properties

Thermal properties such as specific heat and thermal conductivity of carbon nanotubes are determined by the phonons (Popover, 2004). They are very good conductors, The thermal conductivity k of CVD-grown MWCNTs measured from 4 to 300 K (Yi et al., 1999) was found to varied as T^2, similar to that of graphite, and did not show a maximum due to Umklapp scattering. Similar behavior was observed in the measurements of the temperature-dependent thermal conductivity of bundles of SWCNTs from 8 to 350 K (Hone et al., 1999).The measurements of the specific heat of MWCNTs from 10 to 300 K and $1 < T < 200$ K for bundles of SWCNTs with average diameter of 1.3 nm (Yi et al., 1999).

2.3.3 Electrical Properties

Carbon nanotubes have superior and unique electrical properties; they can produce electric current carrying capacity 1000 times higher than copper wires (Collins and Avouris, 2000). For a given (n,m) nanotube, if $n - m$ is a multiple of 3, then the nanotube is metallic, otherwise the nanotube is a semiconductor. Thus all armchair (n=m) nanotubes are metallic, and nanotubes (5,0), (6,4), (9,1), etc. are semi-conducting.

2.3.4 Chemical Reactivity

Carbon nanotube reactivity is directly related to the pi-orbital mismatch caused by an increased curvature. Therefore, a distinction must be made between the sidewall and the

end caps of a nanotube. For the same reason, a smaller nanotube diameter results in increased reactivity. Covalent chemical modification of either sidewalls or end caps has shown to be possible (Niyogi et al., 2002).

2.3.5 Optical Activity

The optical activity of chiral nanotubes disappears if the nanotubes become larger (Thoteson et al., 2001).Therefore, it is expected that other physical properties are influenced by these parameters too. The use of the optical activity might result in optical devices in which CNTs play an important role.

2.3.6 One-Dimensional Transport

Due to their nanoscale dimensions, electron transport in carbon nanotubes will take place through quantum effects and will only propagate along the axis of the tube. Because of this special transport property, carbon nanotubes are frequently referred to as “one-dimensional” in scientific articles.

2.4 Synthesis of Carbon Nanotubes

There are many techniques to produce carbon nanotubes such as Arc discharge, Lazer ablation, condensation-vaporization deposition (CVD) and other methods have been

recently Developed such as solar energy (Journet and Bernier, 1998), the underwater alternating current (AC) electric arc method (Liu and Gao, 2005) and the plasma torch (Chen et al., 2003).

2.4.1 Arc Discharge Method

This method, in which carbon nanotubes were first discovered by Ijima in 1991, is taken place in low pressure He or other neutral atmosphere as shown in Figure 2.3. (Biroet al., 2003).

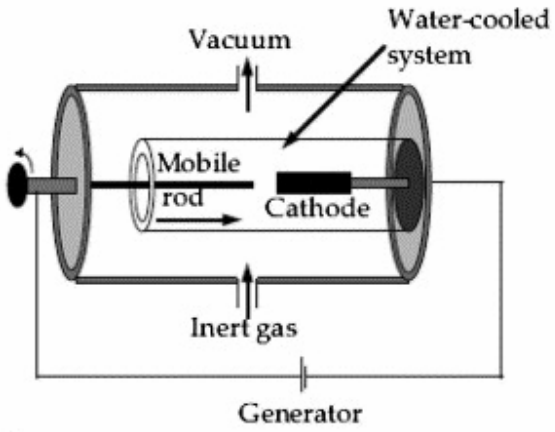


Figure 2. 3 : Experimental setup of an arc discharge apparatus (Biroet al., 2003)

Carbon vapour is generated by arc discharge between two carbon electrodes catalyst and self assemble from the resulting vapour. By adjusting the pressure and catalyst carefully, single- and multi-walled carbon nanotubes with a diameter control to certain degree can be obtained.

2.4.2 Laser Ablation Method

It was discovered by Richard Smalley and co-workers at Rice University in 1995.In this method, a pulsed laser vaporizes a graphite target in a high temperature reactor while an inert gas is bled into the chamber. The nanotubes produce on the cooler surfaces of the reactor, as the vaporized carbon condenses as shown in Figure 2.4. Two kinds of products are possible: multi walled carbon nanotubes or single walled carbon nanotubes (Journet and Bernier, 1998).

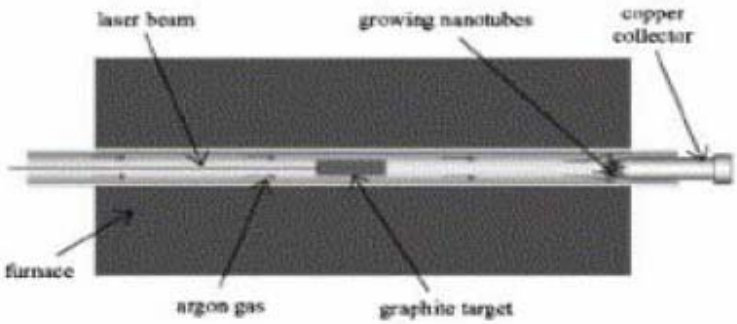


Figure 2. 4 : Schematic drawing of a laser ablation apparatus (Journet and Bernier, 1998)

2.4.3 Carbon Vapour Deposition (CVD)

In the CVD process growth involves heating a catalyst material to high temperatures (500–1000 C^{0}) in a tube furnace using a hydrocarbon gas through the tube reactor over a period of time as shown in Figure 2.5 .The basic mechanism in this process is the

dissociation of hydrocarbon molecules catalyzed by the transition metal and saturation of carbon atoms in the metal nanoparticle .Precipitation of carbon from the metal particle leads to the formation of tubular carbon solids in a sp^2 structure (Muataz et al., 2005).

CVD carbon nanotube synthesis consists of a catalyst preparation step followed by the actual synthesis of the nanotube. The catalyst is generally prepared by sputtering a transition metal onto a substrate and then using either chemical etching or thermal annealing to induce catalyst particle nucleation. Thermal annealing results in cluster formation on the substrate, from which the nanotubes will grow.

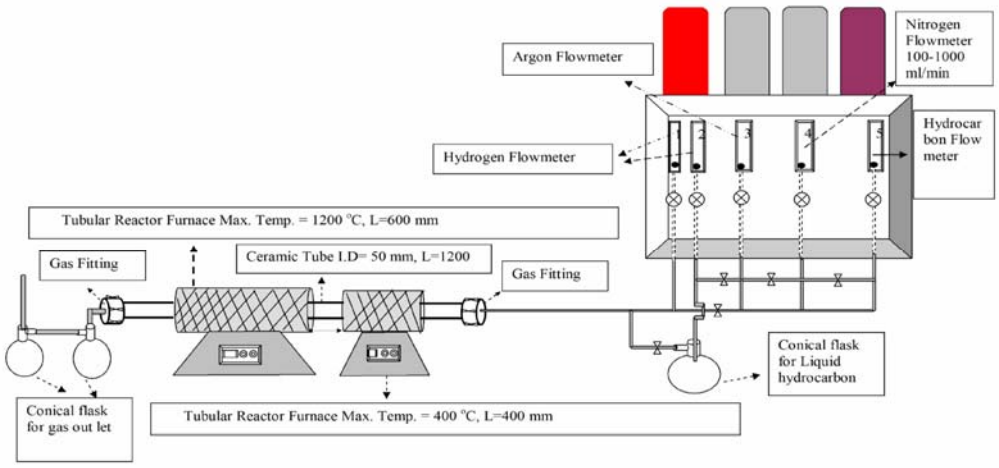


Figure 2. 5 : A schematic diagram of a double-stage CVD apparatus(Muataz et al., 2005)

TABLE 2. 2 : A summary of the major production methods and their efficiency

(Eindhoven University of Technology, 2003)

Method	Arc discharge method	Chemical vapour deposition	Laser ablation (vaporization)
Founder	Ebessen and Ajayan, NEC, Japan 1992	Endo, Shinshu University, Nagano, Japan	Smalley, Rice, 1995
How	Connect two graphite rods to a power supply, place them a few millimeters apart, and throw the switch. At 100 amps, carbon vaporizes and forms hot plasma.	Place substrate in oven, heat to 600°C and slowly add a carbon-bearing gas such as methane. As gas decomposes it frees up carbon atoms, which recombine in the form of NTs.	Blast graphite with intense laser pulses, use the laser pulses rather than electricity to generate carbon gas from which the NTs form, try various conditions until hit on one that produces prodigious amounts of SWNTs.
Typical yield	30 to 90%	20 to 100%	Up to 70%
SWCNT	Short tubes with diameters of 0.6 to 1.4 nm	Long tubes with diameters ranging from 0.6 to 4 nm	Long bundles of tubes (5-20 microns), with individual diameter from 1 to 2 nm
MWCNT	Short tubes with inner diameter of 1 to 3 nm and outer diameter of approximately 10 nm	Long tubes with diameter ranging from 10 to 240 nm	Not very much interest in this technique, as it is too expensive, but MWNT synthesis is possible
Pro	Can easily produce SWNT, MWNTs. SWNTs have few structural defects; MWNTs without catalyst, not too expensive, open air synthesis possible.	Easiest to scale up to industrial production; long length, simple process, SWNT diameter controllable, quite pure.	Primarily SWNTs with good diameter control and few defects. The reaction product is quite pure.
Con	Tubes tend to be short with random sizes and directions; often needs a lot of purification.	NTs are usually MWNTs and often riddled with defects.	Costly technique, because it requires expensive lasers and high power requirement, but is improving.

2.5 Applications

carbon nanotubes (CNTs) have attracted researchers' interest due their exceptional mechanical electrical properties,highly chemical stability and large specific area which are leading to many promising applications, such as chemical sensors (Kong et al., 2000), field emission materials (Tans et al., 1998), catalyst support (Planeix et al., 1994), electronic devices (Saito, 1997), high sensitivity nanobalance for nanoscopic particles (Saito, 1997), nanotweezers (Kim and Lieber, 1999), reinforcements in high performance composites, and as nanoprobes in meteorology and biomedical and chemical investigations, anode for lithium ion in batteries (Lu et al., 2006), nanoelectronic devices (Collins et al., 1997), supercapacitors (Che et al., 1998) and hydrogen storage (Journet et al., 1997). The experiments have shown carbon nanotubes converted to diamond under high pressure and high temperatures with the presence of a certain catalyst (Wang and Cao, 2001).carbon nanotubes have been used in water treatment to remove heavy metals (Stafieja and Pyrzynska, 2007) .

2.5.1 Applications of Carbon Nanotubes in Water Treatment

Clean water is the main concern for the human health and in many parts of the world. The increment in the population of human in many regions of the world, mass consumption and water pollution, the availability of drinking water per capita is inadequate and shrinking . For this reason, water is a strategic resource in the globe, and an important element in many political conflicts. More than 250,000 people die every day from diseases related to the consumption of contaminated water (http://www.who.int). Fresh water, now more precious for its extensive use in agriculture, high-technology manufacturing, and energy production is receiving attention increasingly as a resource requiring better management and sustainable use (Davis and Cornwell, 1998).

The discharge of heavy metals into aquatic ecosystems has become a matter of concern over the last few decades. In view of their high toxicity for human health, heavy metal concentrations in wastewater are restricted by strict standards. The pollutants of serious concern include lead, chromium, mercury, uranium, zinc, copper, etc. due to pollutants carcinogenic and mutagenic nature.

Carbon nanotubes have demonstrated excellent adsorption capacity and many scientists have investigated exploitation of this specific characteristic to develop new tools for environment remediation. Existing of the heavy metals in drinking water will extremely affect the beings health and for this reason a lot of researches have been done and various adsorbents such as activated carbon, iron oxides, filamentous fungal biomass and natural

condensed tannin have been explored by using different method to improve removing heavy metals from the water (Li et al, 2005, (a)).

2.5.2 Chromium and its toxicity

Historically, Louis Nicolas Vauquelin found chromium in 1797. Its name is derived from Greek, *hroma* meaning 'colour', since its different compounds are usually very colorful (Brilly, 2003). Chromium is a polyvalent element, found naturally in the air, soil, water, and lithosphere. The most important natural chromium ore is the mineral chromite $FeCr_2O_4$. Oxidation states ranging from 2+ to 6+ are characteristic of chromium. Divalent chromium is relatively unstable, quickly oxidizing into the trivalent chromium.

Despite the wide range of chromium in the soil and plants, it is rarely found in natural water above the concentration of the natural background, amounting to 1 μg/l, higher concentrations are indicators of antropogenic pollution.

Chromium has the potential to bring about skin infections/ulcerations, nasal tissue damage and upper respiratory lesions, even lung cancer. The whole intake of Cr^{6+} is reduced into Cr^{3+} before penetrating into circulation of blood. Damaged immune system due to Cr^{6+} and Cr^{3+} has also been examined thoroughly (Nordberg et al., 2007). In addition, Cr^{5+} and Cr^{6+} can cause apoptosis, where human lymphocyte comes to death (Katz, 1993).Below listed several potential health effects of the Cr to human in TABLE 2.3.

TABLE 2. 3 : Effects of Cr on the health (Katz, 1993)

Where it can effect	Effect
Eye	Causes eye irritation and possible burns
Skin	May cause skin sensitization, an allergic reaction, which becomes evident upon re-exposure to this material. Exposure may cause irritation and possible burns. Prolonged skin contact may cause injury especially if the skin is abraded.
Ingestion	May cause kidney damage. May cause severe gastrointestinal tract irritation with nausea, vomiting and possible burns
Inhalation	May cause liver and kidney damage. May cause ulceration and perforation of the nasal septum if inhaled in excessive quantities. Causes respiratory tract irritation with possible burns.
Chronic	Prolonged or repeated skin contact may cause sensitization dermatitis and possible destruction and/or ulceration. May cause respiratory tract cancer. May cause liver and kidney damage. Chronic inhalation may cause nasal septum ulceration and perforation.

2.5.3 Lead and its toxicity

Lead is a chemical element in the periodic table that has the symbol Pb and in Latin, it is usually known as plumbum. Lead is a heavy, toxic and malleable poor metal which is normally used in building construction, lead-acid batteries, bullets, solder, pewter, and fusible alloys. In addition, lead is also used in containers for corrosive liquids (such as sulphuric acid) and may be toughened by the addition of a small percentage of antimony or other metals. Like mercury, another heavy metal, lead is a potent neurotoxin which accumulates in soft tissues and bone over time.

Most lead pollutes drinking water through corrosion of lead-containing pipes and plumbing fixtures, especially copper pipes with lead soldered joints. These pipes and fixtures can be in the house or in the drinking water pipelines. Lead in wastewater comes mainly from battery manufacturing, printing, dying and other industries (Nordberg et al., 2007). Other major sources of lead in the environment include lead-based paint, air, soil, household dust and food containers.

Lead has no known benefits to human. Lead has been found to be acute toxic to human beings when present in high amounts in water. It accumulates in human body and will be retained throughout human blood stream. According to the WHO Drinking Water Guidelines, the standard for lead in drinking water is 0.01 mg/L. Lead in drinking water is one of the leading sources of lead in human bodies. It contributes 20 % or more of all lead that people eat, drink, or inhale. Studies have shown that young children, infants and pregnant women are particularly susceptible to unsafe lead levels. In adults, increased levels of lead have been linked to high blood pressure and damaged hearing. Drinking, eating, inhaling even at low level of lead can cause other serious health effects. Excess level of lead (greater than 0.01mg/L) in the human body can cause serious damage to the brain, kidney, high blood pressure, anemia, and cardiovascular (heart and blood vessels) disease. In addition to that, lead can affect the reproductive system in which it will decrease male sperm count. During pregnancy and breast-feeding, lead that is stored in bones is released back into the blood causing an increased levels of lead in blood. Then, it can be transferred from mother to fetus through the placenta or to the infant through

breast-feeding. Lead in wastewater comes mainly from battery manufacturing, printing, painting, dying and other industries as shown in Figure 2.6 .

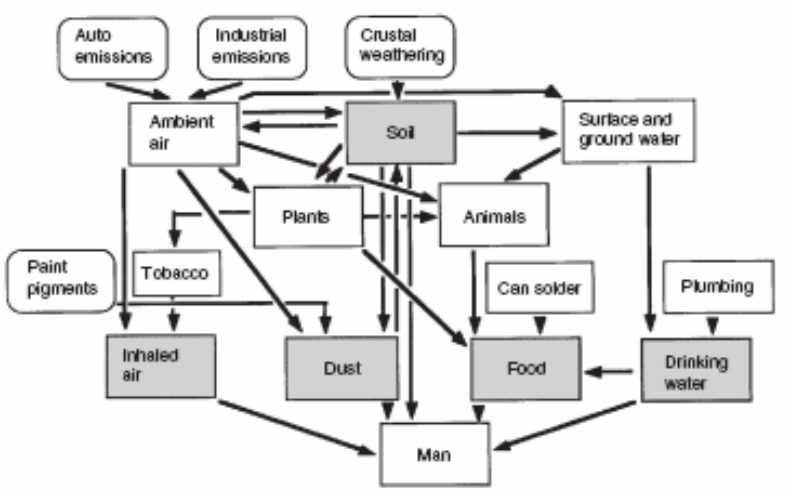


Figure 2.6: Sources and routes of lead exposure in the general population (Nordberg et al., 2007)

Too much lead can damage various systems of the body including the nervous and reproductive systems and the kidneys, and it can cause high blood pressure and anemia. Lead accumulates in the bones and lead poisoning may be diagnosed from a blue line around the gums. Lead is harmful to the developing brains of fetuses and young children and to pregnant women. At very high levels, lead can cause convulsions, coma and death. (Nordberg et al., 2007).

2.6 Removal of Heavy Metals from Water

There are various methods to remove heavy metals such as reverse osmosis, electrodialysis, ultrafiltration, , ion exchange, chemical precipitation, phytoremediation, lime softening, granulated activated Carbon, fly ash, peat, zeolite, biomaterials, manganese oxides, , coagulation, etc. (Ahalya *et al*., 2007, Raoa et al., 2007).

2.6.1 Reverse Osmosis

It is a process in which heavy metals are separated by semi-permeable membrane at a pressure greater than osmotic pressure caused by the dissolved solids in wastewater. The disadvantage of this method is that it is expensive (Ahalya *et al*., 2007).

2.6.2 Electrodialysis

In this process, the ionic components (heavy metals) are separated through the use of semi-permeable ionselective membranes. Application of an electrical potential between the two electrodes causes a migration of cations and anions towards respective electrodes. Because of the alternate spacing of cation and anion permeable membranes, cells of concentrated and dilute salts are formed. The disadvantage is the formation of metal hydroxides, which clog the membrane (Ahalya *et al*., 2007).

2.6.3 Ultrafiltration

They are pressure driven membrane operations that use porous membranes for the removal of heavy metals. The main disadvantage of this process is the generation of sludge (Ahalya *et al*., 2007).

2.6.4 Ion Exchange

In this process, metal ions from dilute solutions are exchange with ions held by electrostatics forces on the exchange resin. The disadvantages include: high cost and partial removal of certain ions (Ahalya *et al*., 2007).

2.6.5 Chemical Precipitation

Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. The large amounts of sludge containing toxic compounds produced during this process are the main disadvantage (Ahalya *et al*., 2007).

2.6.6 Phytoremediation

Phytoremediation is the use of certain plants to clean up soil, sediment, and water contaminated with metals. The disadvantages include that it takes a long time for removal

of metals and the regeneration of the plant for further biosorption is difficult (Ahalya *et al*., 2007).

Hence, the disadvantages like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal has made it imperative for a cost–effective treatment method that is capable of removing heavy metals from aqueous effluents**.**

2.6.7 Adsorbents

In 2002, Li et al. used CNTs which were fabricated by catalytic pyrolysis of the propylene–hydrogen (C_3H_6 : H_2 = 2 : 1) mixture at 750 ^{0}C in a ceramic tube furnace using Ni particles as catalysts. The as-grown CNTs were dispersed in concentrated nitric acid and refluxed at 140 ^{0}C for 1 h to remove most of the catalyst particles. This study has proved that CNTs possess great potential as superior adsorbents for removing lead in and highly dependent on the solution pH value (Li et al., 2002, (b)).

The effects of solution pH, ionic strength and CNT dosage on the competitive adsorption of Pb^{2+} , Cu^{2+} and Cd^{2+} ions were investigated by Li et al. in 2003 , and the competitive adsorption studies showed that the affinity order of three metal ions adsorbed by CNTs is $Pb^{2+} > Cu^{2+} > Cd^{2+}$ (Li et al., 2003 (c)).

In 2003, Li et al. (Li et al., 2003 (d)), (CNTs) were oxidized with H_2O_2, $KMnO_4$ and HNO_3 as shown in Figure 2.7, and the results showed that, that cadmium (II) adsorption capacities for three kinds of oxidized CNTs increase due to the functional groups introduced by oxidation compared with the as-grown CNTs.

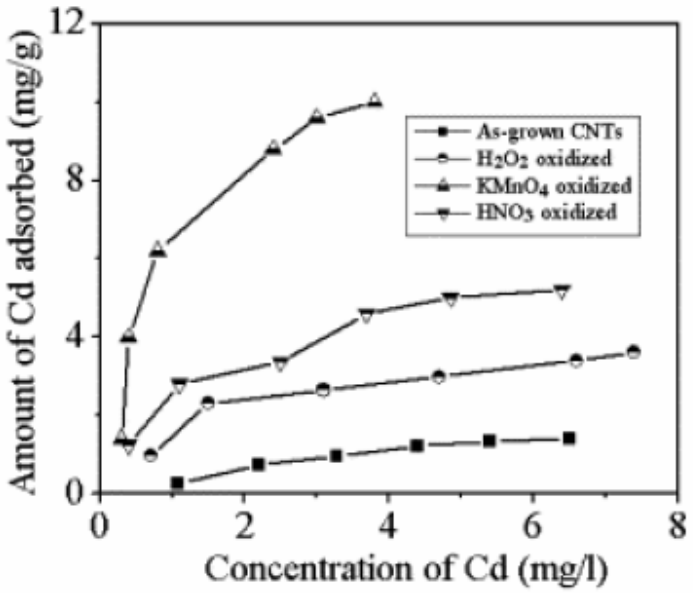


Figure 2. 7 : Adsorption isotherms of Cd (II) adsorbed by CNTs (CNT dosage: 0.05 g per 100 ml; initial pH: 5.5).(Li et al., 2003 (d))

The results of pH and CNT dosage effect on the cadmium(II) adsorption showed that the increase of cadmium(II) adsorption capacity for $KMnO_4$ oxidized CNTs is greater than that of the as-grown, H_2O_2 and HNO_3 oxidized CNTs .

In 2004, Di et al. used Carbon nanotubes (CNTs) to remove chromium(VI) from water and the experiments showed that exceptional adsorption capability and a high adsorption

efficiency for the removal of chromium(VI) ions from water over a broad pH range extending from 4.0 to 7.5 (Di et al, 2004).

In 2006, Lu et al. used Single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) to remove Zn^{2+} from aqueous solution and the results showed that, the amount of Zn^{2+} sorbed onto CNTs increased with a rise in temperature (Lu et al., 2006).

Li et al. used four kinds of CNTs with different morphologies were produced by chemical vapor deposition method and showed that the CNTs with poor quality and morphology have higher lead adsorption capabilities (Li et al. 2006, (e)).

Lu and Liu (in 2006) used Single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) after oxidizing by NaClO solutions and were employed as sorbents to study sorption characteristics of nickel(II) from aqueous solution , and the results indicated that The amount of Ni^{2+} sorbed onto oxidized CNTs increased with a rise in agitation speed, initial Ni^{2+} concentration and solution pH in the range 1–8, but decreased with a rise in CNT mass and solution ionic strength (Lu and Liu, 2006).

In 2008 Di Xu, et al. used Oxidized multiwalled carbon nanotubes MWCNTs) as sorbent to study the sorption characteristic of Pb(II) from aqueous solution as a function of contact time, pH, ionic strength, foreign ions, and oxidized MWCNTs.

The effect of oxidation of activated carbon (AC) with various oxidizing agents (nitric acid, hydrogen peroxide, ammonium persulfate) on preconcentration of metal ions (Cr^{3+}, Mn^{2+} , Pb^{2+} , Cu^{2+} , Cd^{2+} and Zn^{2+}) was investigated by El-Sheikh in 2008.

2.7 Sorption Mechanism

The mechanisms by which the metal ions are sorbed onto CNTs are very complicated and appear attributable to electrostatic attraction, sorption–precipitation and chemical interaction between the metal ions and the surface functional groups of CNTs. However, it have been suggested that the chemical interaction between the metal ions and the surface functional groups of CNTs is the major sorption mechanism (Raoa et al., 2007).

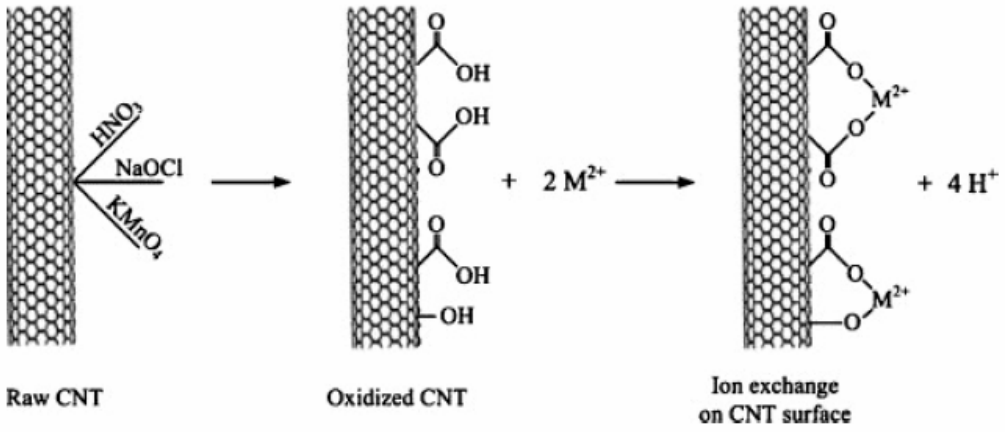


Figure 2.8: Schematic diagram of the major mechanism for sorption of divalent metal ions onto CNT surface (Raoa et al., 2007)

From the literature review, it has been found that, there is no enough information about the effect of pH, contact time, agitation of speed, dosage of CNTs and modification of CNTs on the adsorption of heavy metals such as Pb (II) and Cr (III). Therefore, the effect of these adsorption conditions on the removal of Pb (II) and Cr (III) will be investigated

CHAPTER III

METHODOLOGY

3.1 Characterization of CNTs

The field emission scanning electron microscopy (FE-SEM) was used to characterize the morphology (diameter and the length) of the deposited powder, while the structure was characterized using the transmission electron microscopy (TEM) for the selected sample. The SEM gives good results in characterizing the length and the diameter of the CNT because it is used to scan only the surface of the sample, but it cannot be used to distinguish between the structure of the CNT and other nanoparticles while the TEM is the best way to distinguish between them.

3.2 Preparation of Lead and chromium (III) Stock Solution

The preparation of lead and chromium (III) stock solutions are needed to produce stock solution with concentration of 1 mg/L. Initially, the laboratory glasswares that used in this project were rinsed with 2% of Nitric Acid. This step is very important to remove all the impurities on the glassware and to prevent further adsorption of lead on the wall of the glassware. The stock solution was prepared by pipetting 2mL of lead from lead and chromium (III) standard solution of concentration, 1000 mg/L into volumetric flask (2 L). After that, the deionized water was added to the mark of volumetric flask and mixed

slowly with lead and chromium (III) standard solution by using magnetic stirrer. The pH of the stock solution was adjusted by using 1.0 M Nitric Acid for acid media or 1.0 M NaOH for base media.

3.3 Batch Mode Adsorption Experiment

The experimental of the batch mode adsorption was conducted at room temperature to study the effect of initial solution pH, CNTs dosage, contact time and agitation speed on the adsorption of Pb (II) and Cr (III) ions. Each experiment was conducted in volumetric flask and the initial and final concentrations of Pb (II) and Cr (III) were analyzed by using Inductively Coupled Plasma (ICP).

3.3.1 Effect of pH

The effect of the initial pH solution on the adsorption capacity was investigated by varying the pH of the solution from 4 to 7 for both Pb (II) and Cr (III) ions. The pH of each solution was adjusted to the desired value by 1.0 M Sodium hydroxide for higher pH and 1.0 M Nitric Acid for lower pH. The volumetric flasks containing the mixtures at different pH were shaken for maximum 2 hours. The adsorbent was removed from the solution by filtration method using filter paper.

3.3.2 Effect of Agitation Speed

The speed of the aqueous solution was varied from 50-150 rpm in order to reach to the maximum diffusion of the ions towards the surface of the CNTs. The samples were shaken with mechanical shaker that was controlled by digital controller. Finally, the filtrates samples were analyzed by (ICP).

3.3.3 Effect of CNTs Dosage

The mass of carbon nanotubes were ranging from 1 mg to 160 and 400 mg for lead and chromium respectively. These amounts were inserted into different volumetric flasks containing 50 mL of Pb (II) and Cr (III) aqueous solution at initial concentration (1 mg/L). Then the mixtures were agitated at mild speed for a maximum duration of two hours.

3.3.4 Effect of Contact Time

The adsorption of Pb (II) and Cr (III) ions by Carbon Nanotubes was studied at various time intervals. The experimental work was carried out at different time intervals (10, 20, 30, 40, 60, and 120 min). Finally, the filtrates were analyzed by using (ICP) and the percent removal of Pb (II) and Cr (III) were determined.

3.4 Experimental Design

A systematic data will be designed according to matrix model for lead and chromium as shown in TABLE 3.1.

TABLE 3. 1 : Experiment parameters and its variation

Parameter	Levels
Dosage of CNTs (mg)	5 10
pH	4 5 6 7
Contact Time (min)	10 30 60 120
Agitation Speed (rpm)	50 100 150

3.5 Oxidation the Carbon Nanotubes

MWCNTs were put in a boiling flask. Then concentrated nitric acid (6 M) was added and heated to 120 C^0 by using a magnetic stirring heater for 48 hours. After that, then filtered

by membrane filter and washed by deionized water until pH of filtrate was neutral. Finally, the modified CNTs were dried and kept.

3.6 Adsorption Isotherms Models

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage, and possibility of interaction between the adsorbate species. The Langmuir model assumes that there is no interaction between the adsorbate molecules and the adsorption is localized in a monolayer. The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface, and assumes that different sites with several adsorption energies are involved. In order to model the adsorption behavior and calculate the adsorption capacity for the adsorbent, the adsorption isotherms will be studied. The Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption and it is often expressed as:

$$q = \frac{q_m K_L C_e}{\left(1 + K_L C_e\right)} \tag{1}$$

Where;

$\boldsymbol{q}$ = the adsorption density at the equilibrium solute concentration C_e (mg of adsorbate per g of adsorbent).

$\boldsymbol{C_e}$ = the equilibrium adsorbate concentration in solution (mg/l).

$\boldsymbol{q_m}$ = the maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per g of adsorbent).

$\boldsymbol{K_L}$ = the Langmuir constant related to energy of adsorption (l of adsorbent per mg of adsorbate).

The above equation can be rearranged to the following linear form:

$$\frac{C_e}{q} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{2}$$

The linear form can be used for linearization of experimental data by plotting C_e/q against C_e. The Langmuir constants $\mathbf{q_m}$ and $\mathbf{K_L}$ can be evaluated from the slope and intercept of linear equation.

In addition, we can describe adsorption with Langmuir if there is a good linear fit. If not then maybe some other model will work. Therefore, we can use Freundlich Isotherm.

$$q_e = K_F C_e^{1/n} \tag{3}$$

Where;

$\boldsymbol{q_e}$ is the adsorption density (mg of adsorbate per g of adsorbent)

$\boldsymbol{C_e}$ is the concentration of adsorbate in solution (mg/l)

$\boldsymbol{K_F}$ and $\boldsymbol{n}$ are the empirical constants dependent on several environmental factors and **n** is greater than one.

This equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$Log\ q_e = Log\ K_F + 1/n\ Log\ C_e \quad (4)$$

A plot of Log C_e against Log q_e yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constants can be determined from the slope and the intercept.

3.7 KINETIC MODELING

The study of sorption kinetics is applied to describe the adsorbate uptake rate and this rate evidently controls the residence time of adsorbate at solid liquid interface. In order to evaluate the mechanism of sorption of Pb (II) and Cr (III) by the CNTs, the first-order equation, the pseudo-second-order rate equation and the second-order rate equation are calculated by the below shown equations respectively:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^{\ 2}} + \frac{t}{q_e} \quad (5)$$

Where:

q_e = *sorption capacity at equilibrium*

q_t = *sorption capacity at time (mg/g)*

$\boldsymbol{k_2}$ = *rate constant of the pseudo second-order sorption* ($g.mg^{-1}.min^{-1}$)

t = *time (min)*

The linear plots of $\frac{t}{q_t}$ versus t of the above equation, q_e and k_2 can be determined from the slopes and intercepts.

CHAPTER IV

Results and Discussion

4.1 Characterization of Carbon Nanotubes

High purity of multi wall carbon nanotubes were produced by chemical vapor deposition (CVD) technique. The produced carbon nanotubes were observed by suing field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The diameter of the produced carbon nanotubes were varied from 20-40 nm with average diameter at 24 nm while the length of the CNTs was up to few microns. Figure 4.1 (a) shows the SEM image of carbon nanotubes at low magnification. While Figure 4.2 (b) shows the SEM image of carbon nanotubes at high magnification. From the SEM observation, the product is pure and only carbon nanotubes were observed.

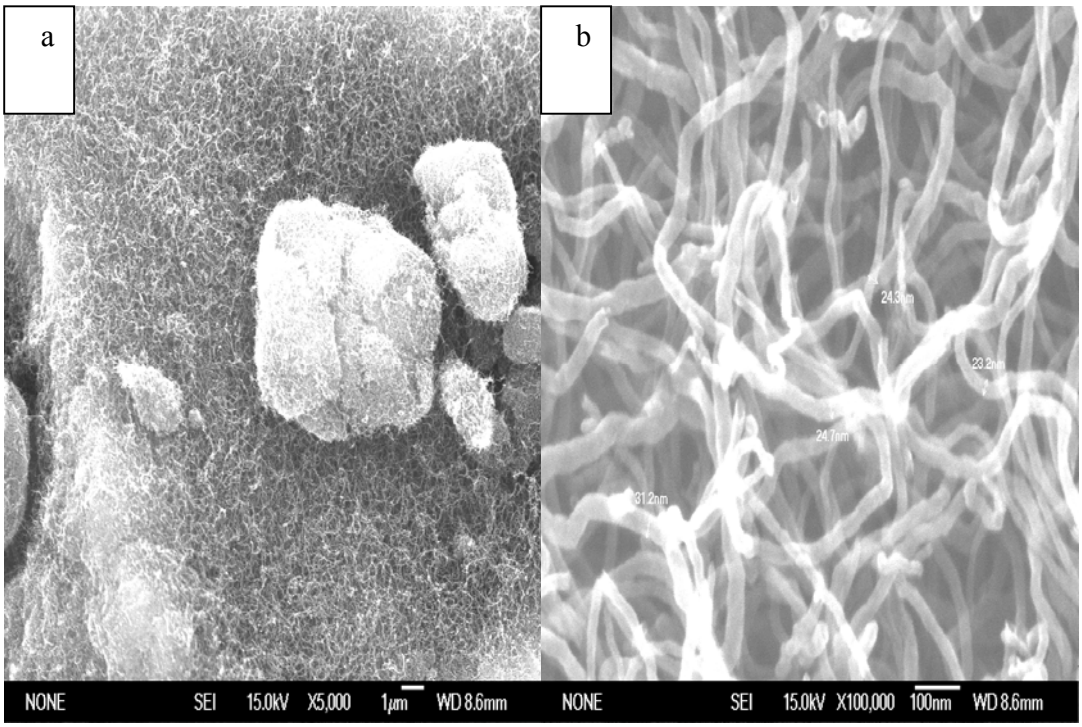


Figure 4. 1 : SEM Images of carbon nanotubes at (a) at low resolution (b) at high resolution

TEM was carried out to characterize the structure of nanotubes (Figure 4.2). To prepare TEM samples, some alcohol was dropped on the nanotubes film, then, these films were transferred with a pair of tweezers to a carbon-coated copper grid. It is obvious from the images that all the nanotubes are hollow and tubular in shape. In some of the images, catalyst particles can be seen inside the nanotubes. TEM images indicate that the nanotubes are of high purity, with uniform diameter distribution and contain no deformity in the structure. While Figure 4.2 (b) shows the High Resolution Transmission Electron Microscope (HRTEM) of the carbon nanotubes. It shows that a highly ordered crystalline structure of CNT is present.

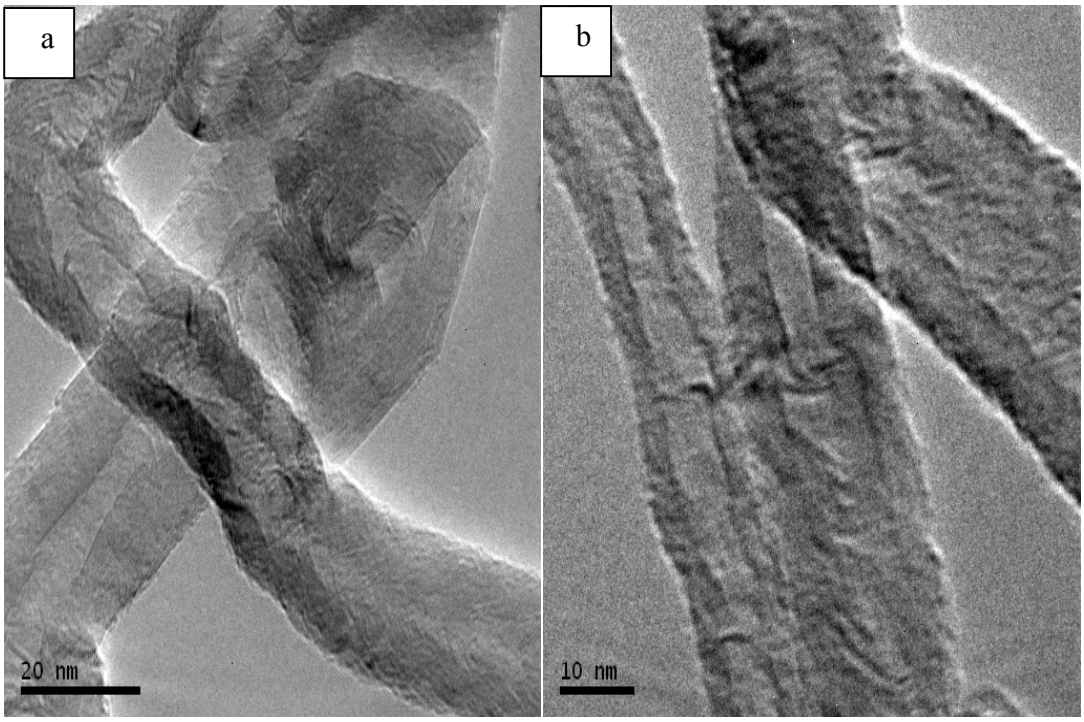


Figure 4. 2 : TEM Images of carbon nanotubes (a) at low resolution (b) at high resolution.

4.2 Removal of Lead and Chromium from Water by Using Modified and Non Modified Carbon Nanotubes

In this project, the effect of pH, agitation speed, modified and non modified CNTs dosage and contact time on the uptake of lead and chromium were investigated to find the optimum conditions for the removal of lead and chromium from water. The percent removal of lead and chromium was determined to measure the adsorption capacity of CNTs.

4.2.1 Removal of lead by using Modified and Non Modified Carbon Nanotubes

The parameters affect on the removal of Pb (II) are:

4.2.1.1 Effect of pH

The pH of aqueous solution is an important variable, which controls the adsorption of ion at the solid-water interfaces. The pH is also said to be an important parameter for the adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of adsorbent and the degree of ionization of the adsorbate during the reaction. When pH of the solution is higher than pH_{PZC} (Point of Zero Charge), the negative charge on the surface provides electrostatic interactions that are favorable for adsorbing cationic species. The decrease of

pH leads to neutralization of surface charge, thus, the adsorption of cations should decrease.

The pH value plays a major role with respect to the adsorption of Pb^{2+} ions on CNTs. The removal of lead by two types of adsorbents (modified and non-modified CNTs) with various pH has been studied. The pH of theses experiments were varied from 4-7. Precipitation will occur between Pb^{2+} and OH^- as the pH exceeds pH 7.0 (Li et al. (a), 2002) To avoid the conflict in the result for the removal of Pb^{2+} by either CNTs or precipitation, our experiments were carried out only under these conditions.

Figure 4.3 shows the effect of pH on the adsorption of Pb^{2+}, which was used as a model of divalent metal ion on raw carbon nanotubes (R-CNTs) and modified carbon nanotubes (M-CNTs). The obtained results indicate that the functional groups introduced by oxidation improve the ion-exchange capabilities of carbon nanotubes and make Pb^{2+} adsorption capacity increase correspondingly. The adsorption of Pb^{2+} species increased with the increase of pH from 4 to 7, but more sharp increase was observed for oxidized CNTs because of the chemical interaction between the metal ions and the surface functional groups such as hydroxyl (-OH), carboxyl (-COOH) and carbonyl (-C=O). These functional groups attached on the surfaces of the CNTs improve their adsorption capability of Pb^{2+} in solution. The low adsorption that took place in acidic region can be attributed in part to competition between H^+ and Pb^{2+} ions on the same sites. Furthermore, the charge of CNTs surface becomes more negative with the increase of

pH, which causes electrostatic interactions and thus results in higher adsorption of metal species.

The result shows that, the adsorption of lead increases with an increase on the pH of the solution from 4 to 7 by using both raw carbon nanotubes (R-CNTs) and modified carbon nanotubes (M-CNTs). The maximum removal of Pb^{2+} by using R-CNTs was 87 percent at pH 7, while the removal of lead at pH 4 and 5 were zero because at acidic region, the surface of the raw carbon nanotubes becomes more neutralize and no negative charge which provides electrostatic interactions that are favorable for adsorbing of Pb^{2+} species. The maximum removal of lead by using M-CNTs was 100 percent at pH 7. At low pH (4 and 5), the removal of lead from the solution by using M-CNTs were 17 and 25 percent respectively. It was reported that at the acidic region there would be a strong competition between the H^{+} and Pb^{2+}, which will reduce the removal capacity of lead by the functional group.

It can be observed that, the removal of lead from water by using modified carbon nanotubes tremendous higher than the raw carbon nanotubes due to the ionization step by the functional group on the surface of CNTs.

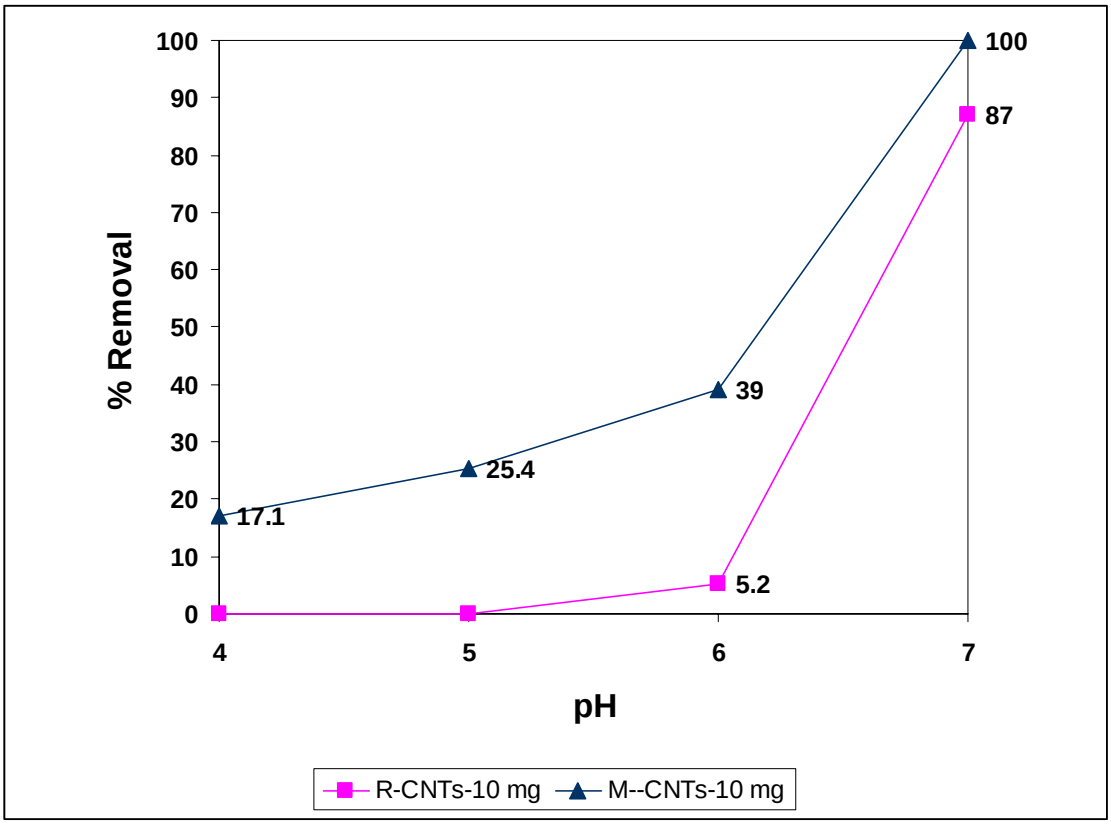


Figure 4. 3 : The effect of pH on percentage removal of lead at 150 rpm, initial concentration = 1 mg/L and Time= 2 hr.

4.2.1.2 Effect of Contact Time

By keeping the carbon nanotubes dosage, agitation speed, and pH at constant values, it was observed that lead adsorption have positive result in terms of time. The amount of Pb^{2+} adsorbed onto both raw carbon nanotubes(R-CNTs) and modified CNTs (M-CNTs) increased rapidly during the beginning 10 minutes. Subsequently, the adsorption rate rises gradually and reaches equilibrium after 30 and 60 minutes for Pb^{2+} adsorption by using (M-CNTs) and (R-CNTs) respectively. The short time required to reach equilibrium suggests that the (M-CNTs) have very high adsorption efficiency and have a great potential in Pb^{2+} adsorbent application.

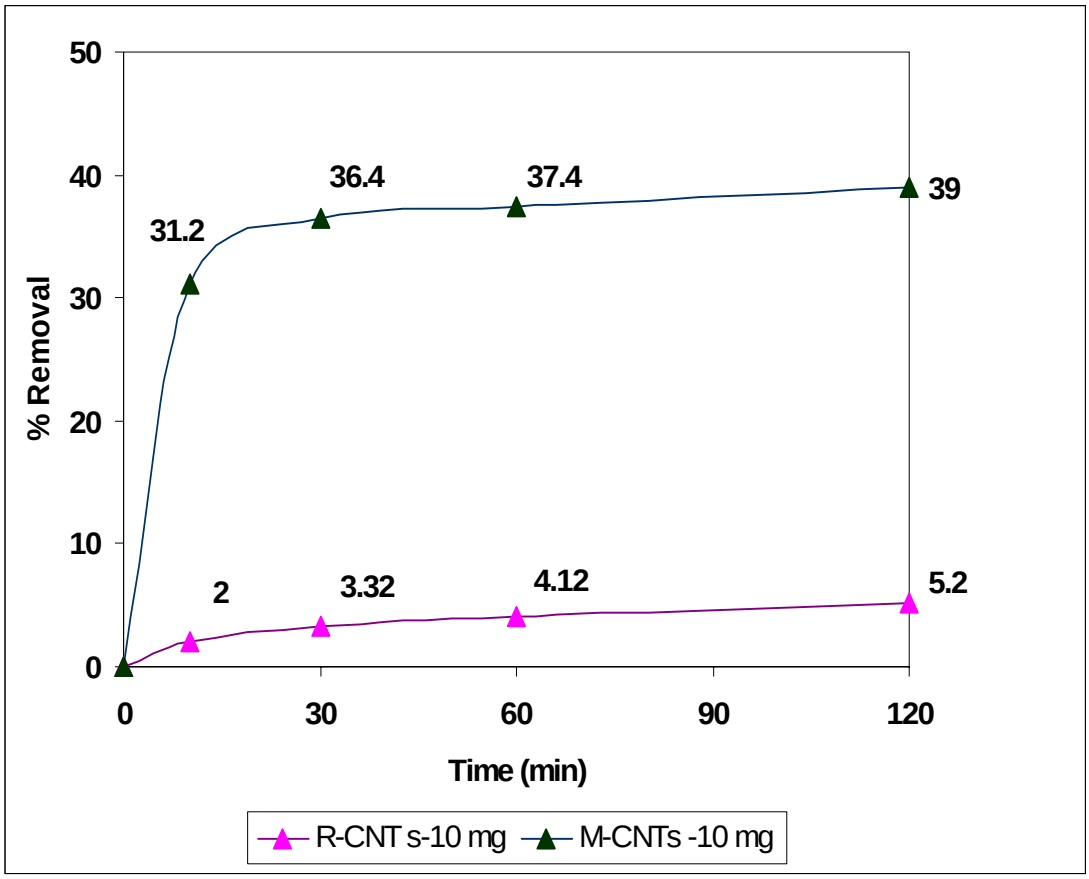


Figure 4. 4 : The effect of time on percentage removal of lead at 150 rpm, pH 6 and initial concentration =1 mg/L

4.2.1.3 Effect of Agitation Speed

The effect of agitation speed on adsorption capacity of lead has been studied by varying the speed of agitation from 50 to 150 rpm. It has been observed that the percentage of lead removal increased slightly by increasing agitation speed. This is due to the fact that, the increase of agitation speed, improves the diffusion of lead ions towards the surface of the adsorbents and decreases the mass transfer resistance when agitation increases, and offers a faster external mass transfer rate of Pb^{2+} and thus gives more adsorption capacity.

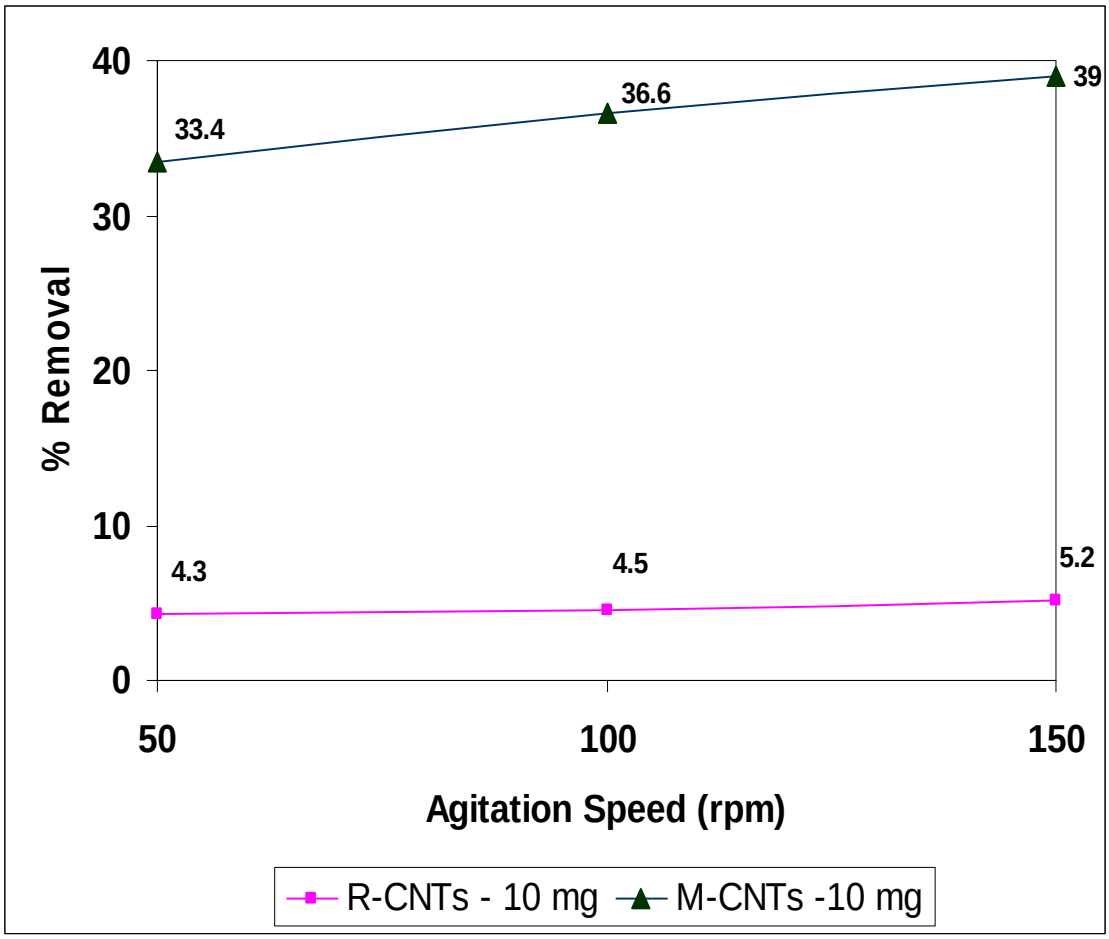


Figure 4. 5 : The effect of agitation speed on percentage removal of lead at pH 6, initial concentration =1 mg/L and time= 2 hr.

4.2.1.4 Effect of CNTs Dosage

The batch adsorption experiments were carried out by using various amounts of R-CNTs and M-CNTs from 5 to 80 mg while the pH, agitation speed and contact time were fixed at 7, 150 rpm and 120 min. respectively. It has been noted that by increase the amount of CNTs into the solution the removal of lead increased. By using M-CNTs the removal, reach up to 100 percent by adding 10 mg while by using R-CNTs the maximum removal of lead was 100 percent after adding 80 mg of adsorbent which could be due to the availability of more sorption sites as shown in Figure 4.6. Apart of that, more experimental study were carried out by using M-CNTs at pH 6 to find the optimum dosage since the maximum removal of lead at pH 7 was 100 at 10 mg. it was found, that the maximum removal of lead was 100 percent when 160 mg of M-CNTs were added as shown in Figure 4.7. Up to a certain value, no further increase in percent sorption of metal ion occurred as an increase in CNT mass.

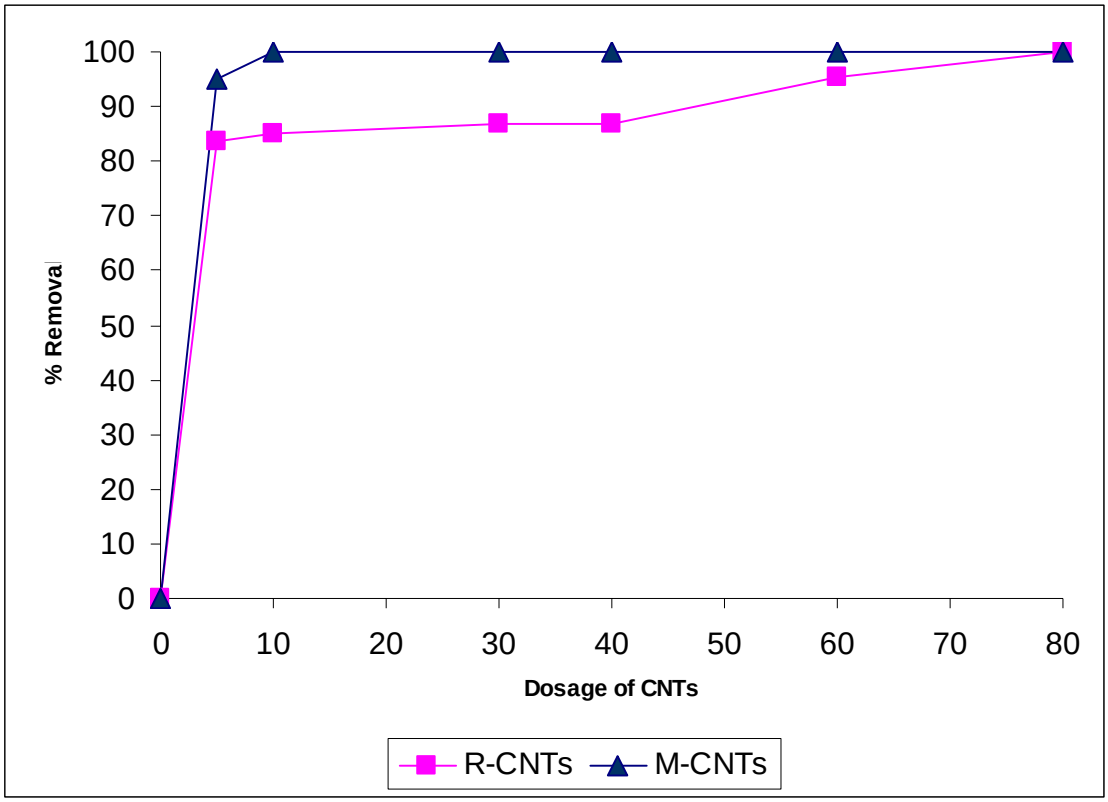


Figure 4. 6 : The effect of dosage of CNTs on percentage removal of lead at 150 rpm , pH 7, initial concentration = 1 mg/L and time = 2 hr.

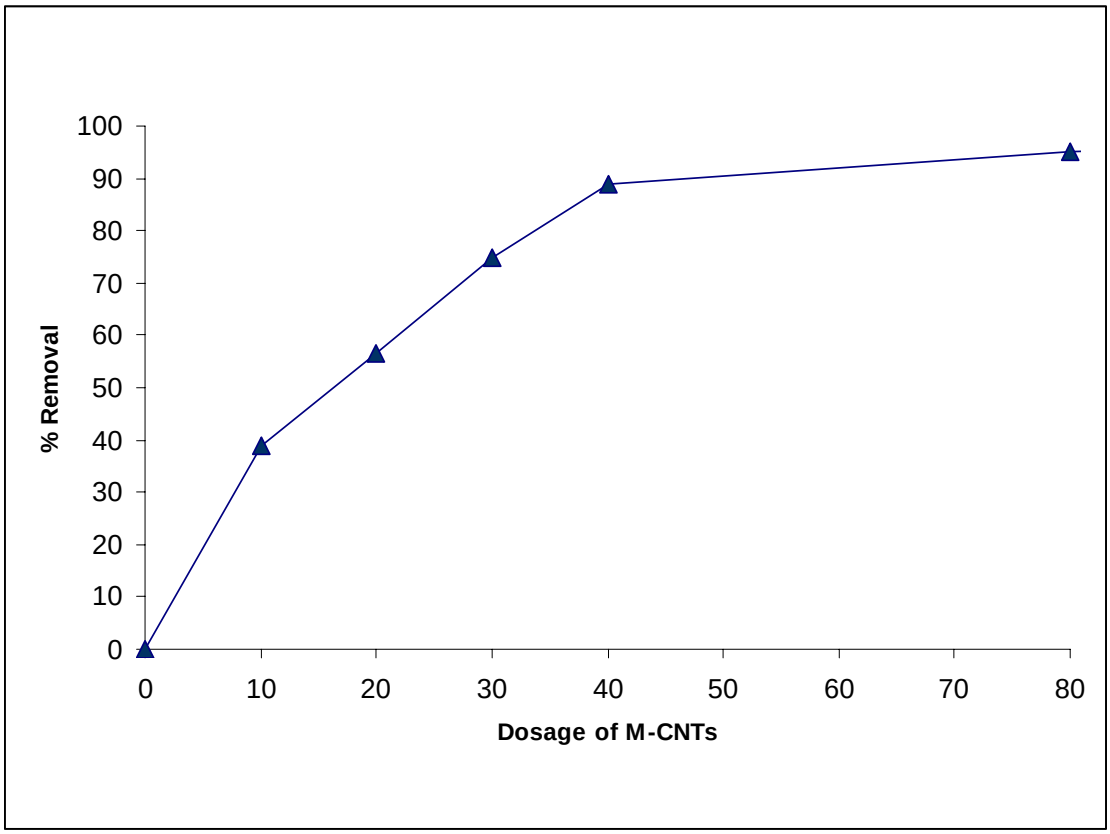


Figure 4. 7 : The effect of dosage of M-CNTs on percentage removal of lead at 150 rpm , pH 6, intial concentarion =1 mg/L and time = 2 hr.

4.2.2 Removal of Chromium from Water by Using Modified and Non Modified Carbon Nanotubes

4.2.2.1 Effect of pH

The removal of chromium by R-CNTs and M-CNTs adsorbents with various pH has been studied. The variations of pH used in the experiments are within the range of 4 to 7. The same phenomenon of the effect of pH was observed. At acidic pH medium, free metal ions exist in solution while surface functional groups present in the protonated form. On the other hand, at basic pH medium, metals are precipitated as their hydroxides while functional groups on adsorbent surface (carboxyl, phenolic, lactonic) exist in the deprotonated form. (El-Sheikh, 2008). Therefore, with the increasing of the pH from 4 to 7 the removal of chromium in the solution will increase and decrease the degree of protonation of the surface which increased the adsorption capacity of the trivalent chromium ion.

There was no removal for chromium (Cr^{3+}) at pH 4 and pH 5 by using raw CNTs. This happened due to the strong competition of H^+ with Cr^{3+} on the adsorption sites. When the pH increased the adsorption of chromium increased slightly. At pH 6 the maximum percentage removal of chromium was about 6 percent, and at pH 7 the removal percentage increased to 7.3 percent by using (R-CNTs).The removal increased to only 10% when (M-CNTs) were used. The weakness of removal of Cr^{3+} refers to In an

aqueous solution Cr^{3+} is in the form $Cr(OH)^{2+}$ or CrO^{-} .Upon hydration the solid surface develops hydroxyl groups which behave as Bronsted acids according to (Shawabkeh, 2006).

$$CSOH_2^{+} \leftrightarrow SC(OH)^{0} + H^{+}$$
$$SC(OH)^{0} \leftrightarrow SC\text{-}O^{-} + H^{+}$$

where $CS–OH^{+2}$ represents the protonated surface hydroxyl groups when the solution acidity is bellow the pH_{ZPC}, $SC–(OH)^{0}$ illustrates the neutral surface at the pH_{ZPC}, while $SC–O^{-}$ is the ionized surface above the pH_{ZPC}.

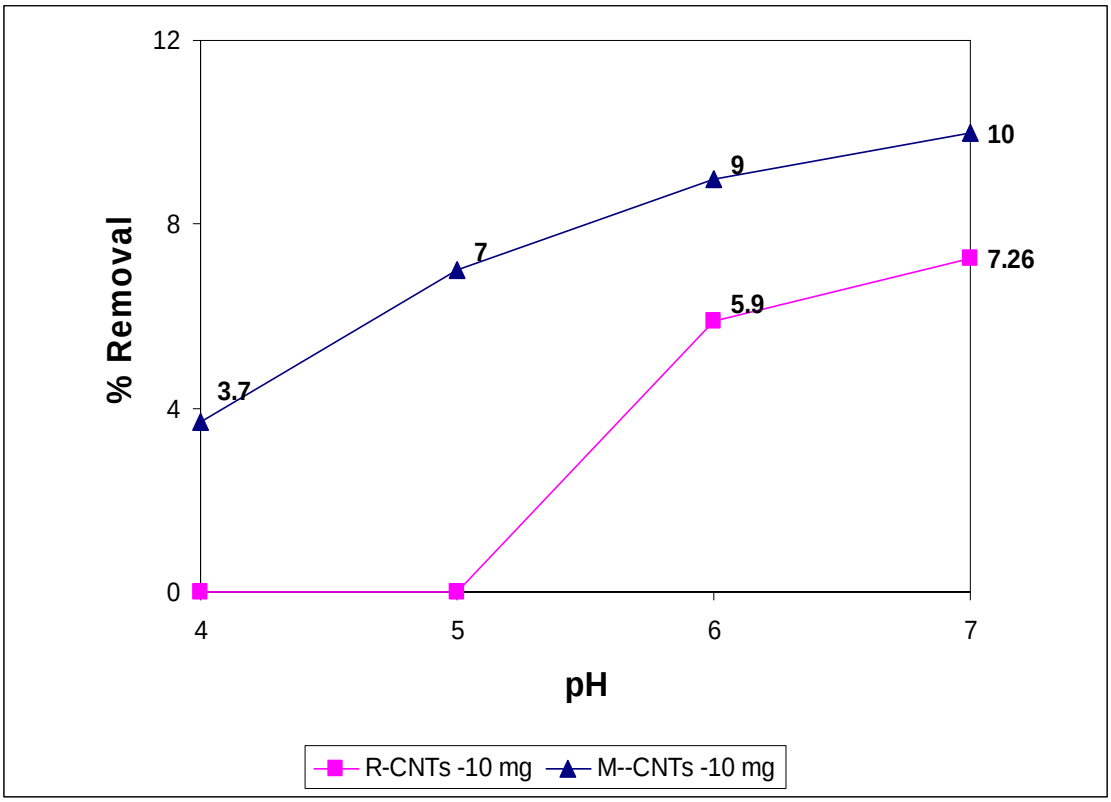


Figure 4. 8 : The effect of pH on percentage removal of chromium at 150 rpm, initial concentration = 1 mg/L and time= 2 hr.

4.2.2.2 Effect of Contact Time

The adsorption behavior of Cr by R-CNT and M-CNTs in relation to the effect of contact time was carried out by varying the equilibrium time from 10 min to 4 h at a Cr concentration of 1 mg/L, a dose of adsorbent of 10 mg/L and at optimum pH of 7. The results showed that the adsorption rate reach to the equilibrium for the R-CNTs and M-CNTs after one-hour and removal was 7 and 10 percent of Cr respectively. It is indicating that by suing M-CNTs, the reaction is fast and the adsorption sites are well exposed as compared to R-CNTs, which has low capacity for adsorption. No h further increase in removal efficiency was observed with time for R-CNTs and M-CNTs after one-hour.

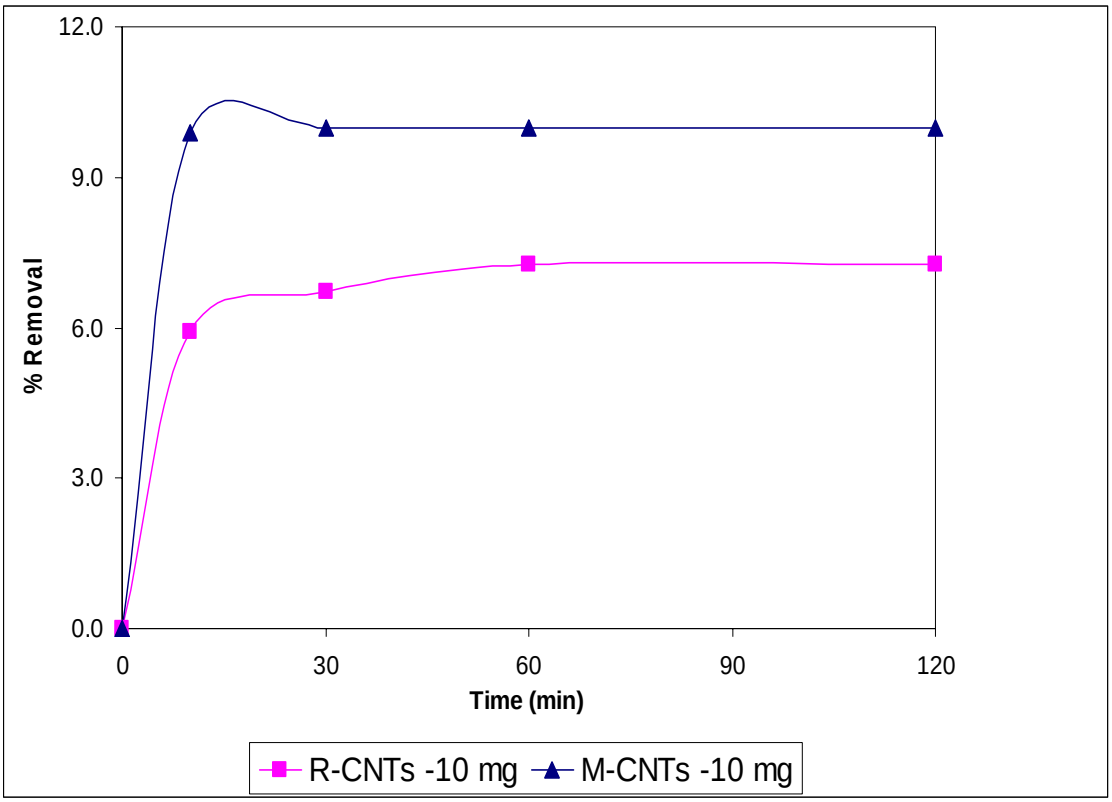


Figure 4. 9 : The effect of contact time on percentage removal of chromium at 150 rpm, pH 7 and initial concentration = 1 mg/L

4.2.2.3 Effect of Agitation Speed

The effect of agitation speed on adsorption capacity of chromium has been studied by varying the speed of agitation from 50 to 200 rpm. It has been observed that the percentage of chromium removal increased slightly with increasing agitation speed. Agitation facilitates proper contact between the metal ions in solution and the CNT binding sites and thereby promotes effective transfer of chromium ions to the carbon nanotubes sites. At 50 rpm and 100 rpm, the adsorption rates monitored were found to be slightly lower than that at 150 rpm. These results indicate that the contact between solids and liquid is more effective at 150 rpm. This is due to the fact that, the increase of agitation speed, improves the diffusion of chromium ions towards the surface of the adsorbents.

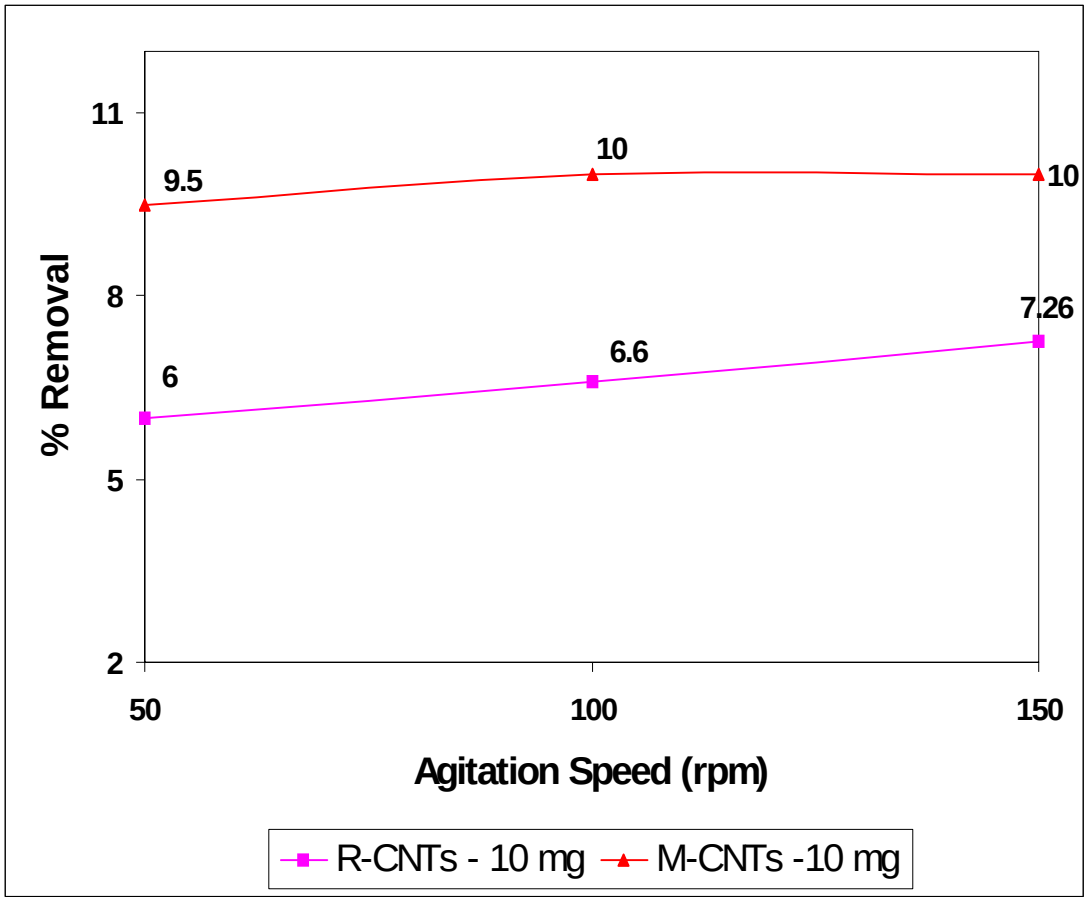


Figure 4. 10 : The effect of agitation speed on percentage removal of chromium at pH 7, intial concentarion= 1 mg/L and time = 2h.

4.2.2.4 Effect of CNTs Dosage

The amount of carbon nanotubes in the water is one of the major factors, which affect the adsorption capacity. The batch adsorption experiments were carried out by using various amounts of M-CNTs from 5 to 400 mg while the pH, agitation speed and contact time were fixed at 7, 150 rpm and 120 min. the results showed that, the adsorption capacity increased with increased in adsorbent dosage. This is expected because the higher the dose of adsorbents in the solution, the greater the availability of exchangeable sites for ions. This suggests that after a certain dose of adsorbent, the maximum adsorption sets in and hence the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of the dose of adsorbent. Therefore, the adsorption capacity for chromium removal is dependent on the adsorbent dosage. It was found, that the maximum removal of chromium was 20 percent when 120 mg of M-CNTs were added. Up to a certain value, no further increase in percent sorption of metal ion occurred as an increase in CNT mass.

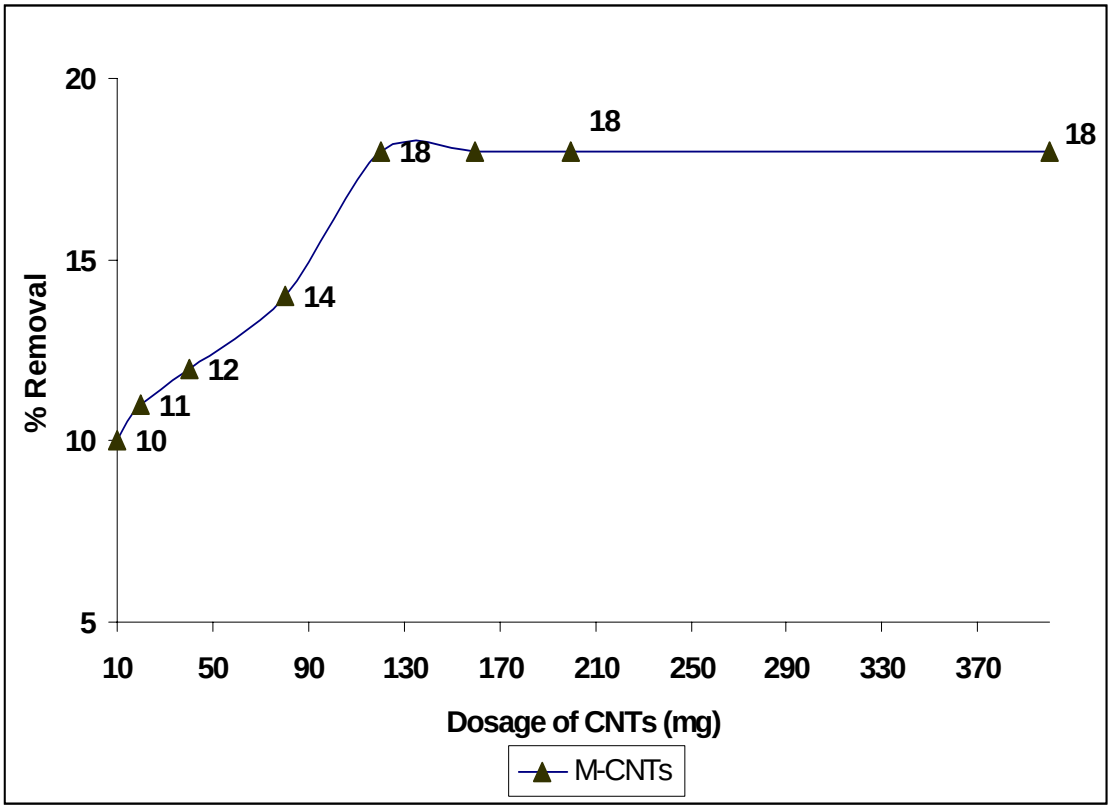


Figure 4. 11 : The effect of agitation speed on percentage removal of chromium at pH 7, initial concentration = 1mg/L and time= 2 hr.

4.3 *Freundlich and Langmuir Isotherms Models*

Freundlich and Langmuir isotherms relate the coverage or adsorption of molecules on a solid surface to gas pressure or concentration of a medium above the solid surface at a fixed temperature.

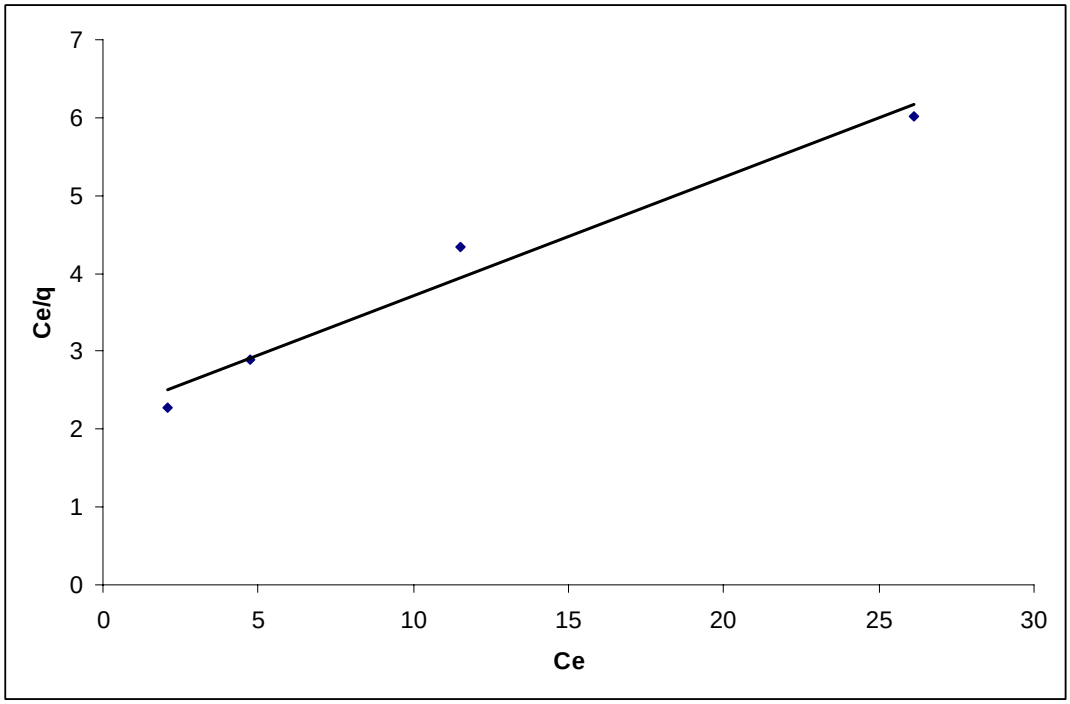
The experimental data for Pb^{2+} and Cr^{3+} adsorption on CNTs at different pH values could be approximated by the isotherm models of Langmuir and Freundlich

4.3.1 Langmuir and Freundlich Adsorption Isotherm Models for Lead

It can be seen from TABLE 4.1 that both Langmuir and Freundlich models show good agreement with the experimental data, with the correlation coefficient values of 0.9731 and 0.9971 respectively. Figures present the linear, Langmuir and Freundlich isotherm plots of Pb (II) adsorption on the M-CNTs at pH 6 as shown in Figure 4.12 (a) and (b). The equilibrium data were fitted very well to all sorption isotherms. Therefore, this indicates the applicability of monolayer coverage of Pb (II) ions on the surface of the adsorbent. This is due to the fact that, CNTs have greater surface area for metal adsorption. The good correlation coefficient of Langmuir and Freundlich isotherm also indicates that Pb (II) ions strongly adsorbed to the surface of M-CNTs. Therefore, it is verified that M-CNTs have great potential to be a good adsorbent for the removal of Pb (II) ions in water treatment.

TABLE 4. 1 : Parameters of Langmuir and Freundlich adsorption isotherm models for lead

Langmuir			Freundlich		
q_m	K_L	R^2	n	K_F	R^2
6.6	0.0704	0.9731	1.6437	0.6041	0.9971



(a)

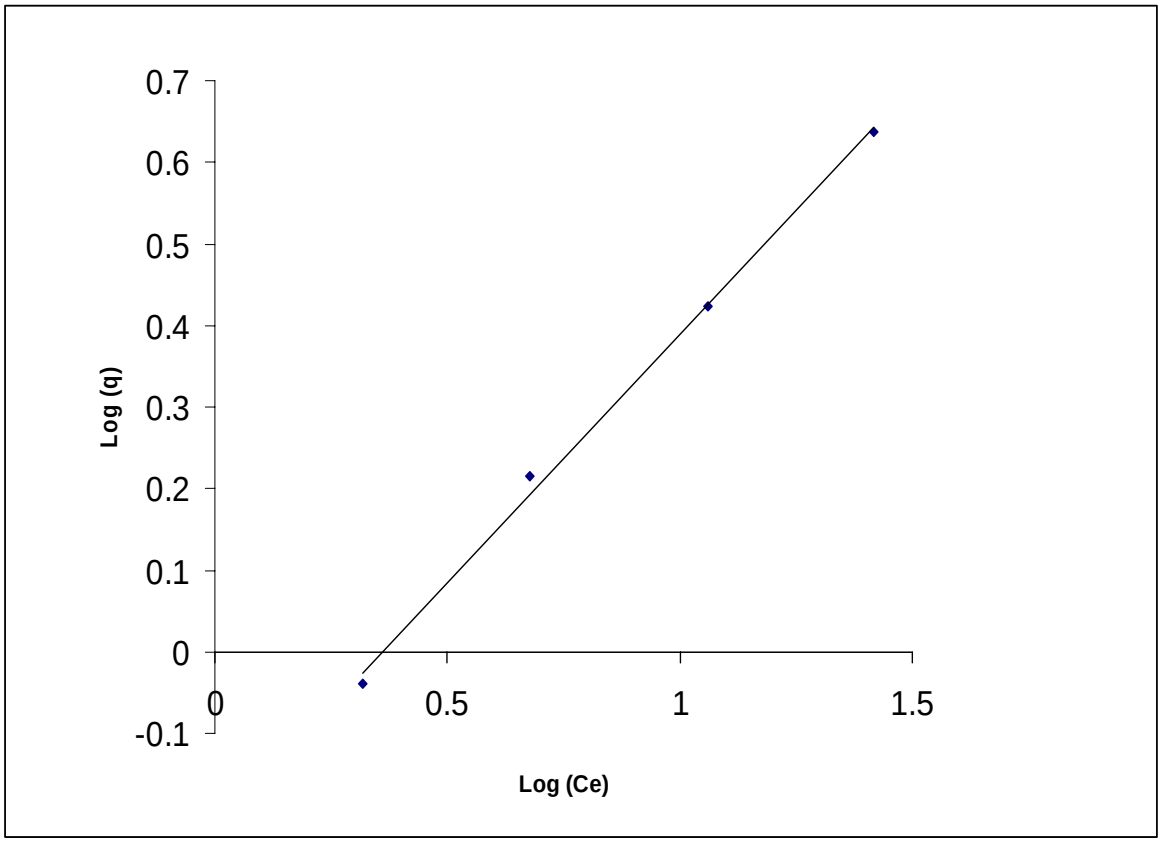


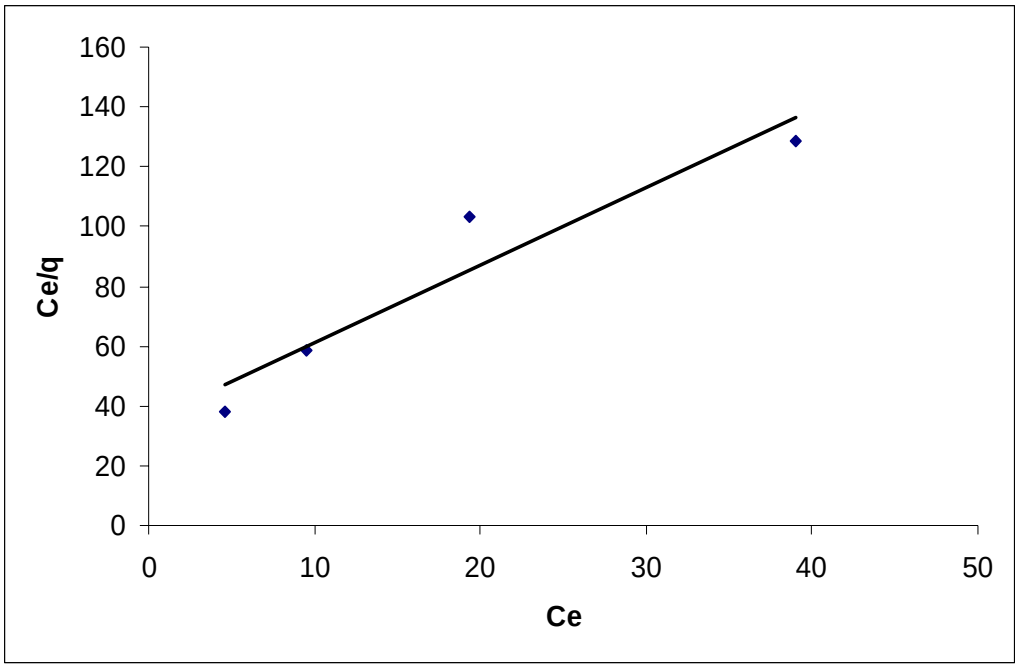
Figure 4. 12 : Adsorption isotherm model for lead (a) Langmuir and (b) Freundlich

4.3.2 Langmuir and Freundlich adsorption isotherm models for chromium

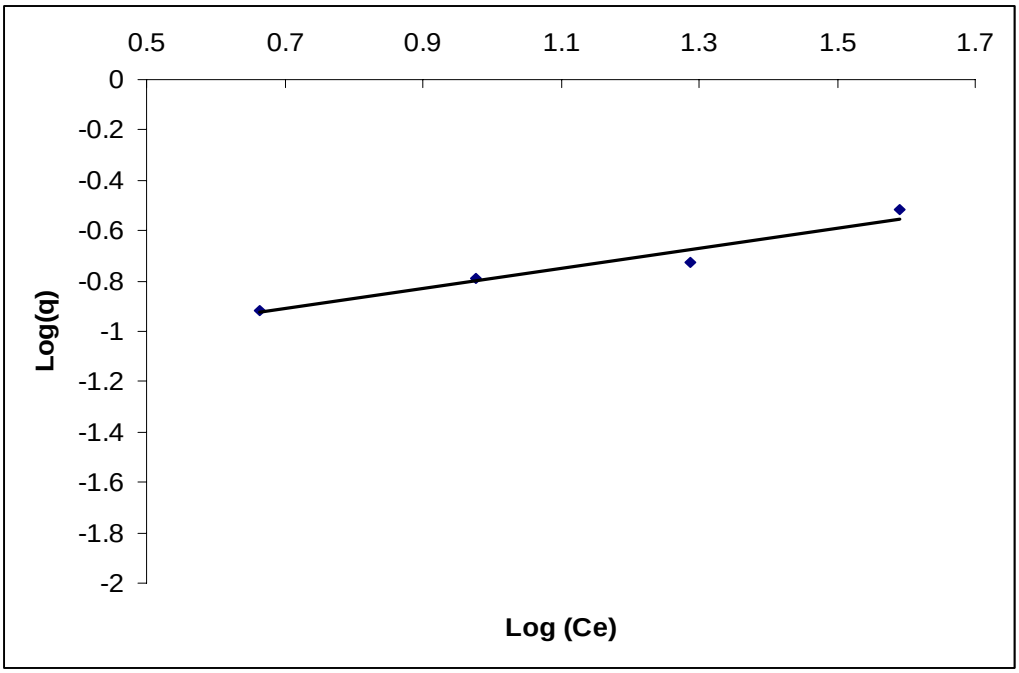
The equilibrium adsorption is important in the design of adsorption systems. Equilibrium studies in adsorption indicate the capacity of the adsorbent during the treatment process. Taking into account that the percentage removal is highest at pH 7, thus, the condition was used to further optimize the adsorption process parameters. The equilibrium curve was modeled in Figure 4.13 (a) and (b)

TABLE 4. 2 : Parameters of Langmuir and Freundlich adsorption isotherm models for chromium

Langmuir			**Freundlich**		
q_m	K_L	R^2	n	K_F	R^2
0.3853	0.0741	0.9089	2.4802	0.0642	0.9494



(a)



(b)

Figure 4. 13 : Adsorption isotherm models for chromium :(a) Langmuir (b) Freundlich

The Langmuir and Freundlich equations were used to describe the data derived from the adsorption of Cr (III) by CNTs over the entire parameters range studied. Based from Figure 4.13, the adsorption capacity (q_e) and adsorption intensity was determined from the slope and intercept of the graph respectively.

Comparison of Langmuir and Freundlich isotherms, Freundlich Isotherm shows better fitting model with higher correlation coefficient (R^2=0.9494) compared to Freundlich Isotherm (R^2=0.9087). Therefore, this indicates the applicability of monolayer coverage of Cr (III) ions on the surface of the adsorbent. This is due to the fact that, CNTs have greater surface area for metal adsorption. The good correlation coefficient of Freundlich isotherm also indicates that Cr (III) ions strongly adsorbed to the surface of CNTs. Therefore, it is verified that CNTs have great potential to be a good adsorbent for the removal of Cr (III) ions in water treatment.

4.4 Kinetics Adsorption Modeling by CNTs

Modeling of kinetic data is fundamental for the industrial application of adsorption since it gives information for comparison among different biomaterials under different operational conditions for designing and optimizing operational conditions for pollutant removal from wastewater systems

The kinetics were investigated by using the information obtained from the effect of dosage (dry-weight basis) at 25°C at three different time intervals up to 120 min. The pseudo first-order kinetic equation was not applicable because R^2 is small comparing to R^2 of pseudo second-order equation .Therefore, the pseudo second-order equation was used in this study in order to investigate the mechanism of adsorption of lead by the CNTs and the potential rate-controlling steps, such as mass transport and chemical reactions .

4.4.1 Kinetics Adsorption Model of Lead

The kinetics adsorption was investigated for lead at pH 6 instead of pH 7 to avoid the conflict the results because of possibility of precipitation of lead at pH 7.The parameters of modeling are shown in TABLE 4.3

TABLE 4. 3 : Kinetic parameters for pseudo second-order model of lead

Adsorbent (10 mg)	q_e (mg/g)	K_2 ($g.mg^{-1}.h^{-1}$)	R^2
R-CNTs	0.30672	8.0439	0.9934
M-CNTs	2	9.7273	0.9998

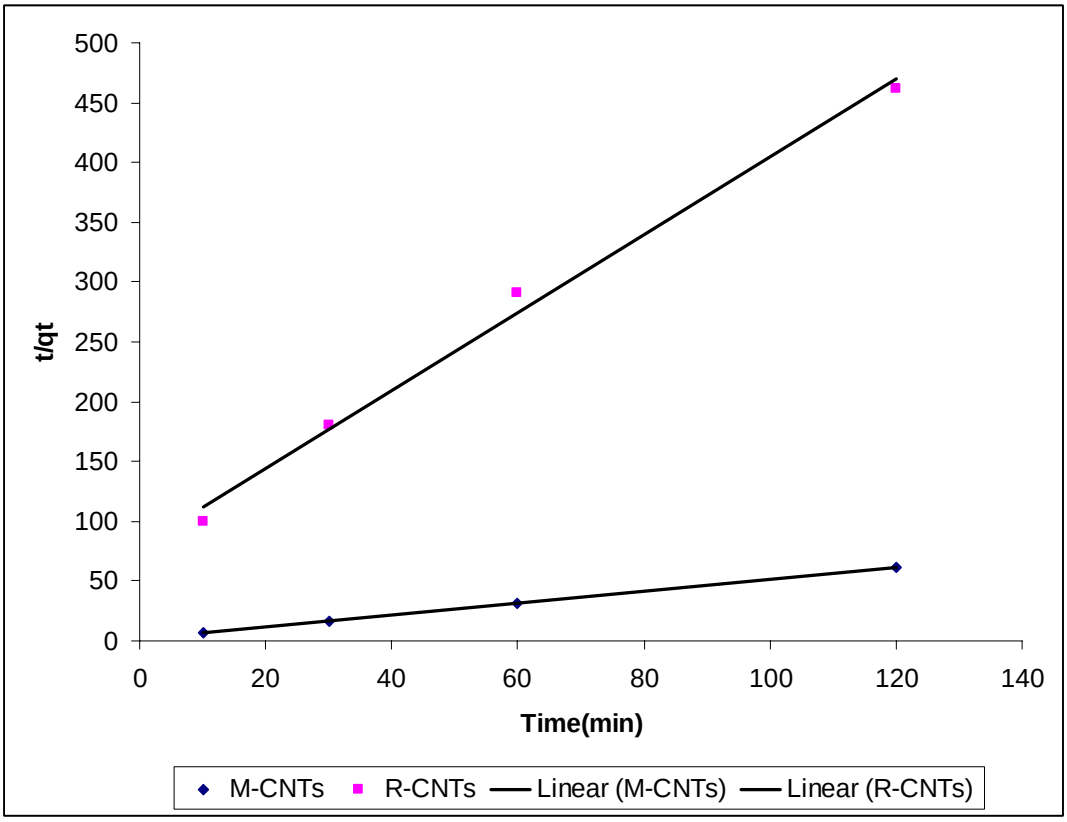


Figure 4. 14 : Pseudo second-order kinetics of Pb (II) using R-CNTs and M-CNTs

The plot of $\frac{t}{qt}$ versus time (Figure 4.14) yields very good straight lines (correlation coefficient, R^2 =0.9934 for R-CNTs and R^2=0.9998 for M-CNTs. The second order-rate constant obtained from this figure are 8.0439 for R-CNTs and 9.7273 ($g.mg^{-1}.h^{-1}$) for M-CNTs. The second order rate constant indicates that time to achieve equilibrium concentration of Pb (II) is less by using M-CNTs compare with R-CNTs . The equilibrium adsorption capacity, q_e obtained from the graph also implies that M-CNTs have higher adsorption capacity (q_e=2 mg/g) is compared to R-CNTs (q_e=0.30672 mg/g).

4.4.2 Kinetics Adsorption Model of Chromium

The kinetics adsorption model has been done for chromium at pH 7.The parameters of modeling are shown in TABLE 4.4

TABLE 4. 4 : Kinetic parameters for pseudo second-order model of chromium

Adsorbent (10 mg)	**q_e (mg/g)**	**K_2 ($g.mg^{-1}.h^{-1}$)**	**R^2**
R-CNTs	0.3718	1.06171	0.9997
M-CNTs	0.5	1.9144	0.9988

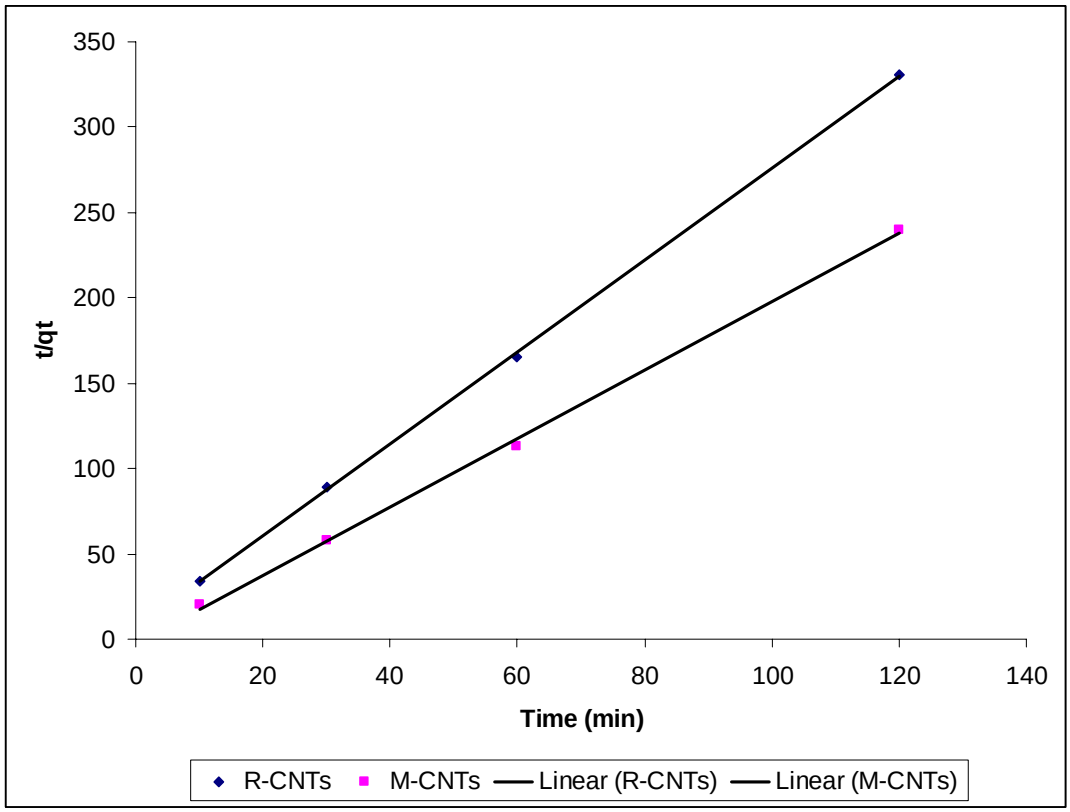


Figure 4. 15 : Pseudo second-order kinetics ofCr (III) using R-CNTs and M-CNTs

By plotting of $\frac{t}{qt}$ versus time (Figure 4.15) yields very good straight lines (correlation coefficient, R^2 =0.9997 for R-CNTs and R^2=0.9988 for M-CNTs. The second order-rate constant obtained from this figure are 1.06171 for R-CNTs and 1.9144 ($g.mg^{-1}.h^{-1}$) for M-CNTs. The second order rate constant indicates that time to achieve equilibrium concentration of Cr (III) is less by using M-CNTs compare with R-CNTs . The equilibrium adsorption capacity, q_e obtained from the graph also implies that M-CNTs have higher adsorption capacity (q_e=0.5 mg/g) is compared to R-CNTs (q_e=0.3718 mg/g).

4.5 Comparative Analysis of Removal Lead and Chromium by CNTs

In this section, a comparison for removing Pb (II) and Cr (III) ions by using CNTs has been done as shown in the TABLE 4.5

TABLE 4. 5 : Comparison of various adsorbents and their uptake of Pb (II) and Cr (III)

Sorbents	Metal Ions	pH	q_m (mg/g)	Reference
R-CNTs	Pb (II)	7	1	Li et al. (2002)
MWCNTs (HNO_3)	Pb (II)	6	2	Xu et al. (2008)
MWCNTs (HNO_3)	Pb (II)	9	0.555	El-Sheikh (2008)
Activated carbon (HNO_3)	Cr (III)		0.178	
MWCNTs (HNO_3)	Pb (II)	6	6.6	This study
	Cr (III)	7	0.3853	

Based from TABLE 4.5, it shows that there are few studies on the removal of Pb (II) and Cr (III) using CNTs. However, the maximum adsorption capacity for each adsorbent is different due to the variation in the operating parameters (pH, agitation speed, dosage, temperature and many more). Thus, this comparative study was conducted to further understand the mechanism of adsorption and compare the types of adsorbents that were previously used to remove Pb (II) Cr (III).

In 2002, Li et al. used CNTs to remove Pb (II) from water and the maximum adsorption capacity (q_m) was 1 mg/g at pH 7. In comparison with Xu et al. used oxidized CNTs oxidized by HNO_3 to remove Pb (II) at pH 6 and he got $q_m = 2$ mg/g . While, in 2008 , El-Sheikh studied both carbon nanotubes and activated carbon (AC) oxidized by HNO_3 at pH 9 and he found the maximum adsorption capacity for M-CNTs and AC are closer to each other ($q_m = 0.555$ mg/g) for Pb (II) and ($q_m = 0.178$ mg/g) for Cr (III).

Finally, in comparison with this study, we have succeeded to get the highest adsorption capacity (q_m) until now .The maximum adsorption capacity for Pb (II) at pH 6 is 6.6 mg/g. While it is 0.3853 for Cr (III) at pH 7.this is refre to the high purity of used CNTs and the oxidization process which has done for 48 h.

CHAPTER VI

CONCLUSION AND RECOMMENDATION

Carbon Nanotubes was found to be efficient for the adsorption of Pb (II) in aqueous solution. The characterization of Pb (II) and Cr (III) uptake showed that the lead and chromium binding is dependent on initial pH, agitation speed, amount of dosage, and contact time. Study of the effects of operational parameters such as pH, CNTs dosage, agitation speed and contact time produced different optimum conditions. Percentage uptake increased with an increased in pH from pH 4 to pH 7. The optimum pH found in this study is pH 7 in which it gave 87% removal of Pb (II) ions by using R-CNTs and 100 % of Pb (II) ions by using M-CNTs from aqueous solution. While for chromium The optimum pH found in this study is pH 7 in which it gave 6 % removal of Cr (III) ions by using R-CNTs and 10 % of Cr (III) ions by using M-CNTs from aqueous solution. The percentage uptake increase slightly with an increase in agitation speed from 50 to 150 rpm, in which 150 rpm gave slightly higher removal for lead and chromium. The percent removal of Pb (II) and Cr(III) was observed to be optimal for higher dosage of CNTs, in which 10 mg of M-CNTs contribute to 100 % removal of Pb (II) ions by M-CNTs compare it with 87 % removal of Pb (II) ions by R-CNTs.

The experimental results were analyzed using Langmuir and Freundlich equations. TABLE 4.4 shows the Langmuir and Freundlich adsorption isotherm constants.

Correlation coefficients (R^2) show that the Langmuir model and Freundlich fitted best to the experimental data for lead while for chromium Langmuir model fitted best to the experimental data. Results from this study are extremely well described by the Langmuir Isotherm in which the highest adsorption capacity obtained from this analysis is 6.6 mg/g for Pb (II) at pH 6 by using M-CNTs .While the highest adsorption capacity of Cr(III) is 0.3853 mg/g . The value obtained demonstrates that CNTs is a good adsorbent for the removal of lead from wastewaters.

Comparative study was conducted at the end of this project to study the effectiveness of other adsorbents that were used to remove Pb (II) and Cr (III). Based from this analysis, it is found out that tree leaves such as common persimmon, mountain laurel, southern magnolia and eastern redbud have great potential to be commercialized as an adsorbent due to its low cost and high availability of material. However, the potential of CNTs should not be underestimated since the application of CNTs as Carbon Nanofilter provides the competitive advantage in terms of cost-effectiveness and scale of operation. Although the cost of CNTs is expensive, but the benefits outweigh the cost since CNTs have high adsorption capacity and can be used for large scale operation compared to other adsorbent. In addition, this study reported that the treatment process only requires mild agitation speed for the removal of Pb (II) and Cr (III), thus it will benefit the industry due to its low power consumption. However, further study is recommended to focus on the cost-effectiveness of CNTs.

Thus, from all these analyses, it is demonstrated that Carbon Nanotubes can be used as an adsorbent for the removal of Pb (II) and Cr (III) ions in water and wastewater treatment. However, further study must be done to further validate the effectiveness of this method in terms of costs and large scale treatment of Pb (II) and Cr (III) in the real industry. Further study and investigation can be done such as:

1. The study of adsorbent dosage should include the particle size characterization and determination of surface area of adsorbent.
2. Study should be conducted using the real wastewater solution from the selected industry to verify its effectiveness on the actual application.
3. Production of Carbon Nanotubes should be conducted to obtain the highest purity of Carbon Nanotubes.
4. The effects of Carbon Nanotubes on human health should be studied thoroughly in order to protect human being from future hazards.
5. Description studies should be carried out to elucidate the mechanism of adsorption and recover the metal loaded adsorbent.
6. Validation study should be conducted to verify the optimization equation that was developed from this study.

Last but not least, the objectives of this project which are to remove Pb (II) and Cr (III) using CNTs and the optimization of process parameters were achieved based on the successful outcome of this project. In addition, the adsorption kinetics of CNTs was developed and the result indicates that there are strong bindings of Pb (II) and Cr (III)

ions on the surface of CNTs. Hopefully, the outcome of this study will benefit the public and protect environment from future degradation.

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APPENDIXES

APPENDIX A

DATA AND RESULTS FOR LEAD

TABLE A4.1: Lead removal % based on pH=6 for raw CNTs

Initial Concentration	Time	Agitation speed	Dosage	Final Concentration	Removal
(mg/L)	(minute)	rpm	(milligram)	(mg/L)	(%)
1	10	50	5	0.996	0.399
1	30	50	5	0.988	1.197
1	60	50	5	0.985	1.463
1	120	50	5	0.968	3.191
1	10	50	10	0.996	0.399
1	30	50	10	0.976	2.394
1	60	50	10	0.967	3.324
1	120	50	10	0.957	4.255
1	10	100	5	0.995	0.532
1	30	100	5	0.976	2.394
1	60	100	5	0.968	3.191
1	120	100	5	0.967	3.324
1	10	100	10	0.988	1.197
1	30	100	10	0.975	2.527
1	60	100	10	0.968	3.191
1	120	100	10	0.951	4.920
1	10	150	5	0.989	1.064
1	30	150	5	0.968	3.191
1	60	150	5	0.985	3.856
1	120	150	5	0.956	4.388
1	10	150	10	0.980	1.995
1	30	150	10	0.967	3.324
1	60	150	10	0.959	4.122
1	120	150	10	0.948	5.186

TABLE A4.2: Lead removal % based on pH=7 for raw CNTs

Initial Concentration	Time	Agitation speed	Dosage	Final Concentration	Removal
(mg/L)	(minute)	rpm	(milligram)	(mg/L)	(%)
1	10	50	5	0.584	41.6
1	30	50	5	0.442	55.8
1	60	50	5	0.412	58.8
1	120	50	5	0.377	62.3
1	10	50	10	0.393	60.7
1	30	50	10	0.363	63.7
1	60	50	10	0.328	67.2
1	120	50	10	0.293	70.7
1	10	100	5	0.388	61.2
1	30	100	5	0.368	63.2
1	60	100	5	0.361	63.9
1	120	100	5	0.294	70.6
1	10	100	10	0.314	68.6
1	30	100	10	0.302	69.8
1	60	100	10	0.216	78.4
1	120	100	10	0.203	79.7
1	10	150	5	0.371	63
1	30	150	5	0.325	67.5
1	60	150	5	0.179	82.1
1	120	150	5	0.165	83.5
1	10	150	10	0.245	76.4
1	30	150	10	0.236	76.4
1	60	150	10	0.183	81.7
1	120	150	10	0.132	85
1	120	150	30	0.15	86.8
1	120	150	40	0.13	87
1	120	150	60	0.045	95.5
1	120	150	80	0	100

TABLE A4.3: Lead removal % based on pH=4 for modified CNTs

Initial Concentration	Time	Agitation speed	Dosage	Final Concentration	Removal
(mg/L)	(minute)	rpm	(milligram)	(mg/L)	(%)
1	10	50	10	0.911	8.94
1	30	50	10	0.866	13.41
1	60	50	10	0.859	14.12
1	120	50	10	0.853	14.71
1	10	100	10	0.875	12.50
1	30	100	10	0.858	14.24
1	60	100	10	0.855	14.47
1	120	100	10	0.842	15.76
1	10	150	10	0.859	14.12
1	30	150	10	0.856	14.35
1	60	150	10	0.855	14.47
1	120	150	10	0.829	17.06

TABLE A4.4: Lead removal % based on pH=5 for modified CNTs

Initial Concentration	Time	Agitation speed	Dosage	Final Concentration	Removal
(mg/L)	(minute)	rpm	(milligram)	(mg/L)	(%)
1	10	50	10	0.878	12.20
1	30	50	10	0.846	15.40
1	60	50	10	0.856	14.40
1	120	50	10	0.812	18.80
1	10	100	10	0.865	13.53
1	30	100	10	0.844	15.60
1	60	100	10	0.813	18.70
1	120	100	10	0.782	21.80
1	10	150	10	0.85	15.00
1	30	150	10	0.8	20.00
1	60	150	10	0.764	23.60
1	120	150	10	0.746	25.40

TABLE A4.5: Lead removal % based on pH=6 for modified CNTs

Initial Concentration	Time	Agitation speed	Dosage	Final Concentration	Removal
(mg/L)	(minute)	rpm	(milligram)	(mg/L)	(%)
1	10	50	10	0.769	23.10
1	30	50	10	0.742	25.80
1	60	50	10	0.704	29.60
1	120	50	10	0.666	33.40
1	10	100	10	0.710	29.00
1	30	100	10	0.673	32.70
1	60	100	10	0.65	35.00
1	120	100	10	0.634	36.60
1	10	150	10	0.688	31.20
1	30	150	10	0.636	36.40
1	60	150	10	0.626	37.40
1	120	150	10	0.61	39.00
1	120	150	10	0.619	38.10
1	120	150	20	0.435	56.50
1	120	150	40	0.251	74.90
1	120	150	80	0.112	88.80
1	120	150	120	0.05	95.00
1	120	150	160	0	100.00

APPENDIX D

Removal percentage of chromium in water by using R-CNTs and M-CNTs

TABLE A4.6: Chromium removal % based on pH=6 for raw CNTs

Initial Concentration	Time	Agitation speed	Dosage	Final Concentration	Removal
(mg/L)	(minute)	rpm	(milligram)	(mg/L)	(%)
1	10	50	5	0.996	0.399
1	30	50	5	0.984	1.600
1	60	50	5	0.979	2.100
1	120	50	5	0.968	3.200
1	10	50	10	0.990	1.000
1	30	50	10	0.979	2.100
1	60	50	10	0.972	2.800
1	120	50	10	0.958	4.200
1	10	100	5	0.981	1.900
1	30	100	5	0.979	2.100
1	60	100	5	0.976	2.400
1	120	100	5	0.955	4.500
1	10	100	10	0.975	2.500
1	30	100	10	0.973	2.700
1	60	100	10	0.970	3.000
1	120	100	10	0.955	4.800
1	10	150	5	0.980	2.000
1	30	150	5	0.976	2.400
1	60	150	5	0.972	2.800
1	120	150	5	0.946	5.400
1	10	150	10	0.970	3.000
1	30	150	10	0.972	2.800
1	60	150	10	0.968	3.200
1	120	150	10	0.941	5.900

TABLE A4.7: Chromium removal % based on pH=7 for raw CNTs

Initial Concentration (mg/L)	Time (minute)	Agitation speed rpm	Dosage (milligram)	Final Concentration (mg/L)	Removal (%)
1	10	50	5	0.965	3.348
1	30	50	5	0.965	3.348
1	60	50	5	0.967	3.482
1	120	50	5	0.962	3.752
1	10	50	10	0.960	4.000
1	30	50	10	0.960	4.156
1	60	50	10	0.957	4.291
1	120	50	10	0.950	5.908
1	10	100	5	0.961	3.617
1	30	100	5	0.964	3.752
1	60	100	5	0.962	3.752
1	120	100	5	0.964	5.235
1	10	100	10	0.961	4.022
1	30	100	10	0.960	4.156
1	60	100	10	0.958	4.561
1	120	100	10	0.954	6.582
1	10	150	5	0.948	5.235
1	30	150	5	0.944	5.639
1	60	150	5	0.948	5.235
1	120	150	5	0.948	5.639
1	10	150	10	0.927	5.91
1	30	150	10	0.933	6.72
1	60	150	10	0.941	7.26
1	120	150	10	0.934	7.26

TABLE A4.8: Chromium removal % based on pH=4 for modified CNTs

Initial Concentration	Time	Agitation speed	Dosage	Final Concentration	Removal
(mg/L)	(minute)	rpm	(milligram)	(mg/L)	(%)
1	10	50	10	1.000	0.00
1	30	50	10	0.989	1.10
1	60	50	10	0.978	2.20
1	120	50	10	0.972	2.80
1	10	100	10	0.974	2.60
1	30	100	10	0.972	2.80
1	60	100	10	0.969	3.10
1	120	100	10	0.970	3.00
1	10	150	10	0.971	2.90
1	30	150	10	0.971	2.90
1	60	150	10	0.963	3.70
1	120	150	10	0.963	3.70

TABLE A4.9: Chromium removal % based on pH=5 for modified CNTs

Initial Concentration	Time	Agitation speed	Dosage	Final Concentration	Removal
(mg/L)	(minute)	rpm	(milligram)	(mg/L)	(%)
1	10	50	10	0.97	3.00
1	30	50	10	0.962	3.80
1	60	50	10	0.946	5.40
1	120	50	10	0.941	5.90
1	10	100	10	0.966	3.40
1	30	100	10	0.954	4.60
1	60	100	10	0.942	5.80
1	120	100	10	0.941	5.90
1	10	150	10	0.95	5.00
1	30	150	10	0.95	5.00
1	60	150	10	0.939	6.10
1	120	150	10	0.93	7.00

TABLE A4.10: Chromium removal % based on pH=6 for modified CNTs

Initial Concentration	Time	Agitation speed	Dosage	Final Concentration	Removal
(mg/L)	(minute)	rpm	(milligram)	(mg/L)	(%)
1	10	50	10	0.947	5.30
1	30	50	10	0.942	5.80
1	60	50	10	0.937	6.30
1	120	50	10	0.931	6.90
1	10	100	10	0.945	5.50
1	30	100	10	0.932	6.80
1	60	100	10	0.925	7.50
1	120	100	10	0.924	7.60
1	10	150	10	0.931	6.90
1	30	150	10	0.928	7.20
1	60	150	10	0.922	7.80
1	120	150	10	0.91	9.00

TABLE A4.11: Chromium removal % based on pH=7 for modified CNTs

Initial Concentration	Time	Agitation speed	Dosage	Final Concentration	Removal
(mg/L)	(minute)	rpm	(milligram)	(mg/L)	(%)
1	10	50	10	0.911	8.90
1	30	50	10	0.905	9.50
1	60	50	10	0.903	9.70
1	120	50	10	0.901	9.90
1	10	100	10	0.903	9.70
1	30	100	10	0.901	9.90
1	60	100	10	0.9	10.00
1	120	100	10	0.9	10.00
1	10	150	10	0.901	9.90
1	30	150	10	0.897	10.30
1	60	150	10	0.894	10.60
1	120	150	10	0.9	10.00
1	180	150	10	0.897	10.30
1	180	150	20	0.892	10.80
1	180	150	40	0.881	11.90
1	180	150	80	0.861	13.90
1	180	150	120	0.822	17.80
1	180	150	160	0.971	17.80
1	180	150	200	0.951	17.80
1	180	150	400	0.821	17.90

APPENDIX B

TABLE B.1: Materials for the experiment.

MATERIALS
1. Sample Adsorbents • Raw carbon nanotubes (R-CNTs) • Modified carbon nanotubes (R-CNTs) 2. Stock Pb (II) solution 3. Stock Chromium (III) Solution 4. 0.1 N Sodium Hydroxide 5. 6 M nitric acid 6. Deionized water

APPENDIX C

TABLE C.1: Equipment for the Experiment

No.	Equipments
1.	Transmission Electron Microscopy, TEM
3.	Scanning Electron Microscopy, SEM
4.	Inductively coupled plasma (ICP)
5.	Mechanical Shaker
6.	pH Indicator
9.	Magnetic Stirring Heater
10	Sonicator
10.	100 ml Conical flasks
11.	1000 mL Volumetric flasks
12.	1-5 mL, petites
13.	Balancer
14.	Test Tube rack
15.	Scott Bottles (100 mL)

APPENDIX D

Experimental Figures

FigureD.1: Photograph of Batch Mode Adsorption Experiment

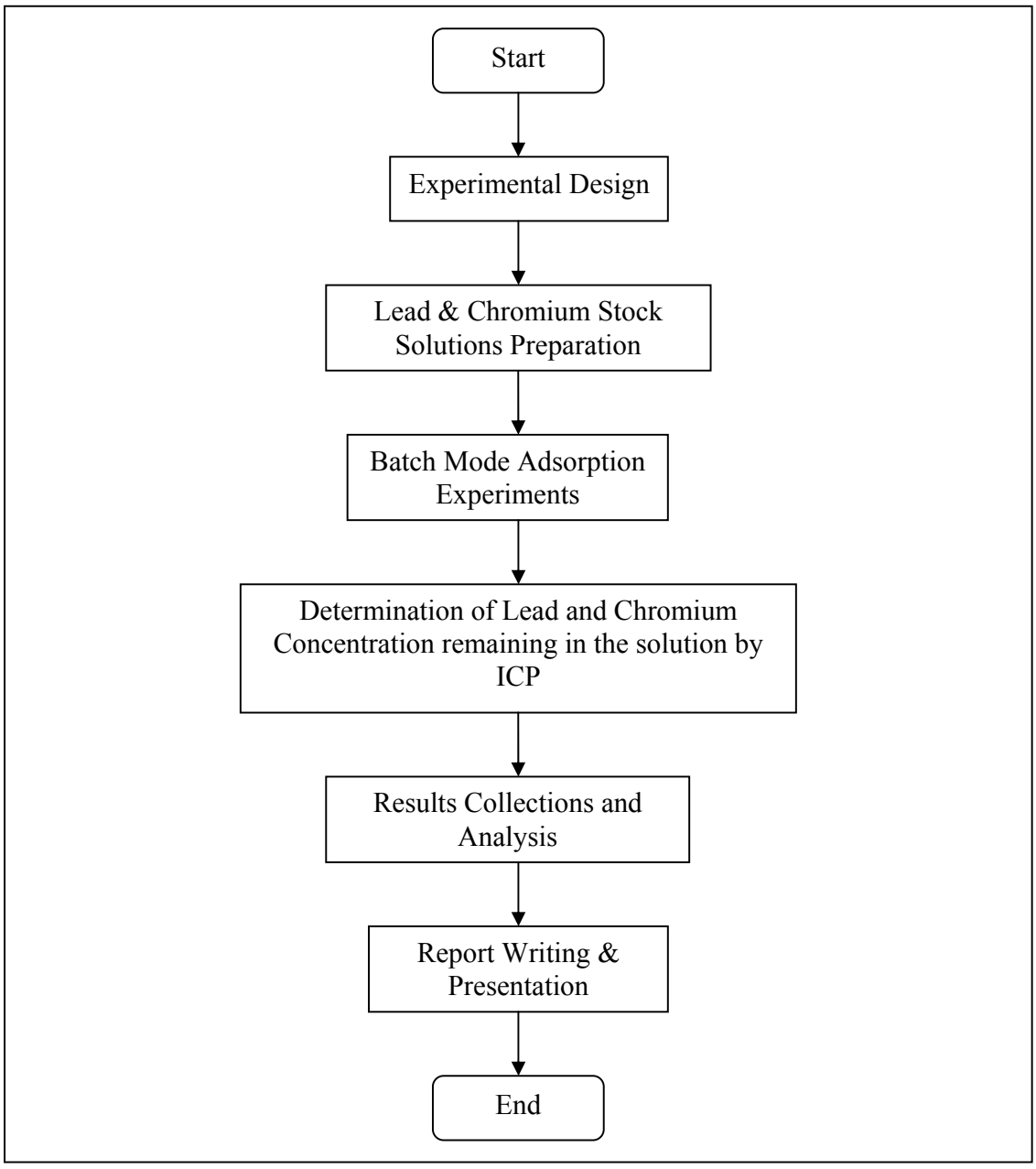
Figure D.2 :A photograph of SEM JEOL 6400

Figure D.3: A photograph of TEM Hitachi H-7100

Figure D.4: A Sonicator

APPENDIX E

Experimental Flowchart for Final Year Project



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